

Attachment 8

CHLE-015: Summary of Chemical Effects Testing in 2012 for STP GSI-191 License Submittal

PROJECT DOCUMENTATION COVER PAGE

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Title: Summary of Chemical Effects Testing in 2012 for STP GSI-191 License Submittal		
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Summary/Purpose of Analysis or Calculation:

Corrosion/Head Loss Experiment (CHLE) tests were performed to support the risk-informed resolution of GSI-191 at the South Texas Project Nuclear Operating Company (STP). This document presents the results of testing, calculations, and analysis conducted during 2012 to evaluate the extent to which chemical precipitates may contribute to additional blockage on emergency core cooling system (ECCS) strainers beyond what is caused by non-chemical debris.

The results of this analysis suggest that it is reasonable to conclude that chemical precipitates are unlikely to have an additional contribution to strainer blockage following ruptures on pipes up to 6 inches in diameter. Although the results are more preliminary, this outcome may also be extended to breaks on pipes up to 15 inches in diameter.

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1	11/14/2012	Draft document for internal review
2	11/26/2012	Addressed internal review comments. Submitted to NRC for public meeting.
3	1/15/2013	Addressed internal review comments, added material from LBLOCA test and changed name of document.

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Introduction

The purpose of this report is to describe the results from calculations, experiments, and analysis conducted as part of the Corrosion/Head Loss Experimental (CHLE) program. The CHLE testing is being conducted at the University of New Mexico (UNM) to investigate the effects of chemical precipitates on Emergency Core Cooling System (ECCS) strainer blockage under realistic conditions for the South Texas Project (STP) in support of the risk-informed resolution of Nuclear Regulatory Commission (NRC) Generic Safety Issue (GSI) 191. Three objectives within the CHLE program are to determine, for realistic conditions, (1) the rates of corrosion and release of chemical reactants and products from materials present in the containment building at a nuclear power plant (2) whether or not chemical precipitates can form in the post loss-of-coolant accident (LOCA) environment, and (3) the effect on ECCS strainer debris bed head loss from any observed chemical products.

Four sets of tests are described in this report:

1. A series of tests were performed to examine the characteristics and performance of two types of fiberglass debris beds when prepared with varying amounts of debris and when subjected to chemical precipitants that are formed using the WCAP-16530-NP protocol [1]. The two types of fiber bed preparation methods included disaggregating fibers by pressure-washing using the protocol advocated by Nuclear Energy Institute (NEI) [2] or chopping fibers in a blender. This testing program included 14 tests and was conducted from 22 May 2012 to 07 June 2012.
2. Two multi-day tests that evaluated the response of two types of debris beds when exposed to aluminum nitrate injected directly into the tank solution to simulate precipitation that may occur when aluminum enters the solution at a slow rate, as it would do via corrosion. These tests were conducted from 28 June 2012 to 24 July 2012.
3. A 30-day experimental simulation of a LOCA on a 6-inch pipe under conditions that are representative of the STP plant. For the purposes of the risk-informed resolution of GSI-191, pipe breaks have been divided into small break LOCAs (SBLOCA, 2-inch breaks and smaller), medium break LOCAs (MBLOCA, 2-inch to 6-inch breaks), and large break LOCAs (LBLOCA, greater than 6-inch breaks). This test simulated the upper bound of the MBLOCA class. The test included aluminum specimens in a corrosion tank and fiberglass debris in three parallel head loss columns. This test was conducted from 22 Aug 2012 to 25 Sept 2012.
4. A 30-day experimental simulation of a LOCA on a 15-inch pipe (an intermediate-sized LBLOCA) under conditions that are representative of the STP plant. In addition to the materials present in the medium break LOCA, this test also included a concrete specimen, galvanized steel coupons, and zinc granules. This test was conducted from 5 Oct 2012 to 8 Nov 2012.

In addition, this report summarizes earlier testing of the ECCS Sure-FlowTM strainer module subjected to prototypical debris from the STP plant by Alden in 2008 [3,4]. The Alden testing was conducted using bounding conditions representative of a design basis LOCA, based on calculations performed for STP [5] for this condition. The Alden testing forms the prior basis for

the effect of chemical precipitates on head loss at the STP plant and is a useful point of comparison for the results from the CHLE program.

The 30-day MBLOCA and LBLOCA tests are the primary tests with regard to the effect of chemical precipitates on the resolution of GSI-191 under risk-informed conditions. The results of the other two testing campaigns provide background information on the utility of using various types of beds for chemical effects testing and are discussed at the end of this report.

Review of ECCS Sure-Flow™ Strainer Module Testing for the STP Plant

Testing was conducted at Alden Research Laboratory, Inc. over a 3-day period in July 2008 to evaluate the head loss across a Performance Contracting, Inc (PCI) Sure-Flow™ strainer module subjected to prototypical debris from the STP plant [3,4]. The test module had a screen area of 91.44 ft². The tank had a volume of 1830 gallons and flow was recirculated at 353 gpm, which provided a screen velocity of 0.0086 ft/s and a circulation time of 5.2 minutes. Two tests were conducted, one with no debris that established the baseline head loss through a clean strainer, and a second one with a combination of non-chemical debris and chemical precipitates. The target temperature for the tests was 120 °F but the measured temperature was somewhat lower. At 0.0086 ft/s, the normalized head loss (normalized to 116.3 °F) through the clean strainer was 0.092 ft (1.1 inches). During the test with debris addition, the water temperature ranged from 102 °F to 112 °F (38.8 to 44.4 °C).

The quantity of debris was scaled to the surface area of the screens in the STP plant with two ECCS trains in operation. The ECCS screens in the STP plant have a surface area of 1815.5 ft² each, for a total area of 3,631 ft². Thus, the quantity of debris in the Alden test was scaled to be 2.52 percent of the quantity in a design-basis LOCA at STP. The quantity of non-chemical debris in the Alden test included 6.6 lbm of Nukon fiberglass in various sizes, 8.55 lbm of Knauf thermal wrap fiberglass insulation in various sizes, 0.95 lbm of Microtherm powder, 4.65 lbm of Marinite Board powder, 3.65 lbm of latent particulate dirt and dust, 34.45 lbm of tin, 14.95 lbm of pulverized acrylic coatings, and 2.75 lbm of acrylic chips. These materials were added to the test system in 4 batches over about 3 hours and water was allowed to circulate overnight before chemical precipitates were added to the system. The head loss peaked at about 5 ft of water column after the non-chemical debris was added and declined to about 4 ft by the following morning.

The quantity of chemical precipitates added during the test was determined using calculations for a design-basis LOCA at the STP plant [5]. Calculations based on the WCAP-16530-NP protocol predict the release of 63.06 kg of calcium, 208.85 kg of silicon, and 82.92 kg of aluminum when the water in the pool is at the maximum level and the spray systems are operated continuously for 30 days in a design basis LOCA [5]. The design basis for the quantity of precipitates is summarized in Table 1. The amount of silicon and aluminum released into solution is reduced when the water is at the minimum level, which decreases the amount of sodium aluminum silicate (NaAlSi₃O₈) and increases the amount of aluminum oxyhydroxide (AlOOH) that is formed. By selecting the maximum water level to determine NaAlSi₃O₈ formation and the minimum water level to determine AlOOH formation, the test evaluated a quantity of aluminum

precipitates that were greater than could be generated from the aluminum available under any single condition.

As permitted in WCAP-16530-NP, Alden substituted AlOOH precipitate for $\text{NaAlSi}_3\text{O}_8$ precipitate (on a mass basis). Using the recipes in WCAP-16530-NP, the AlOOH was prepared using 117.2 kg of aluminum nitrate $[\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$ and 37.6 kg of sodium hydroxide (NaOH) added into 450.6 gallons of tap water. The calcium phosphate $[\text{Ca}_3(\text{PO}_4)_2]$ precipitate was prepared using 7.27 kg of calcium acetate $[\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}]$ and 10.48 kg of trisodium phosphate ($\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$) added into 226 gallons of tap water.

Precipitate addition started after water had been circulating through the strainer covered with the non-chemical debris for approximately 18 hours. The AlOOH precipitate was added in 20 batches and the $\text{Ca}_3(\text{PO}_4)_2$ precipitate was added in 18 batches. The test plan called for the AlOOH and $\text{Ca}_3(\text{PO}_4)_2$ precipitates to be added separately with typically 1 or 2 pool turnovers between one batch and the next. The first 23 batches of precipitates were added to the tank over about 5.5 hours on Day 2 of the test. Water continued to circulate overnight (about 17 hours), and then the remaining 15 batches of precipitates were added over about 5.3 hours on Day 3 of the test.

The chemical addition resulted in the ECCS strainer module being thoroughly coated with chemical precipitates, as shown in Figure 1 [4]. The maximum normalized head loss (excluding clean strainer head loss and piping losses) at 0.0086 ft/s with chemical precipitates was 8.75 feet (normalized to 116.5 °F). Immediately prior to chemical addition, the head loss through the strainer loaded with non-chemical debris was about 4.0 feet. Thus, the additional head loss due to chemical precipitates was 4.75 ft or an increase of 2.2 times over the head loss without chemical precipitates.

Table 1 – Quantities of Precipitates used for Preparing the Prototype Strainer Module Testing for STP

Precipitate	Quantity (kg)	Water volume
$\text{NaAlSi}_3\text{O}_8$	649.5	Maximum
AlOOH	64.9	Minimum
$\text{Ca}_3(\text{PO}_4)_2$	162.7	Maximum

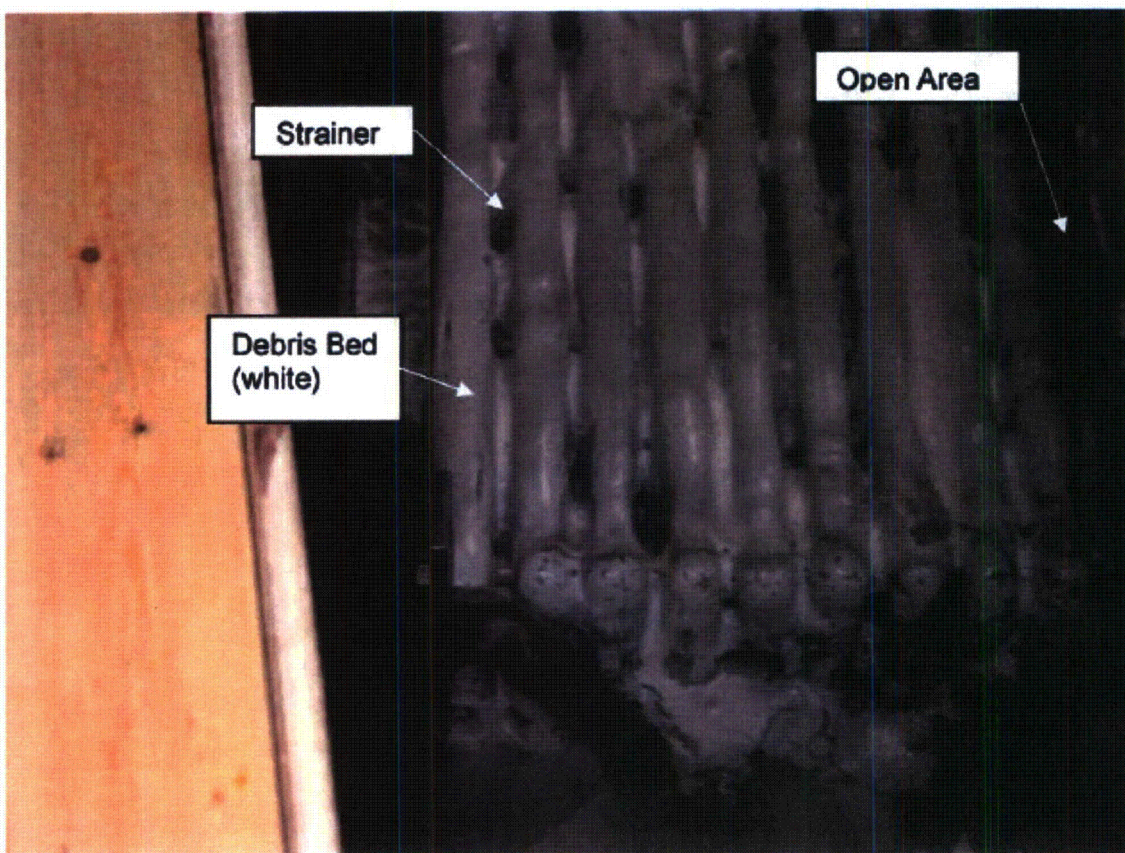


Figure 1 – Precipitates covering a PCI Sure-Flow™ strainer module after testing for a design basis LOCA at the STP. In this test, the loading rate on the strainer was 990 g/m^2 for aluminum and 190 g/m^2 for calcium (reproduced from [4]).

To compare the results of experimental testing programs to full-scale performance, the chemical quantities can be scaled based on either pool volume and strainer area. Dividing chemical quantities by pool volume defines the concentration of chemicals in solution, which is relevant because the quantity of precipitates that form is affected by the relationship between actual concentration and the solubility limitations of the relevant precipitates. Dividing chemical quantities by the screen area is relevant because the head loss will be influenced by the actual precipitate loading on the screen. Based on pool volume, the chemical additions in the Alden test resulted in an aluminum concentration of $1,220 \text{ mg/L}$ as Al and a calcium concentration of 240 mg/L as Ca. Based on screen loading, the chemical quantities resulted in a screen loading of 990 g/m^2 of Al and of 190 g/m^2 of Ca.

Calculated Release of Aluminum, Silicon, and Calcium in a Medium Break LOCA under Realistic Conditions

The quantity of precipitates used in the Alden testing as discussed in the previous section was based on a design basis LOCA and several conservative assumptions. The calculated amounts of

precipitates change when the quantities of materials in containment and assumptions are based on realistic conditions. A summary of the quantities of aluminum, silicon, and calcium predicted by the WCAP-16530-NP calculation procedure to be released into solution is shown in Table 2. The results presented in this table demonstrate that a more realistic assessment would generate lower concentrations of chemicals in solution. Comparing Case 0 and Case 4 demonstrates that using realistic values for the water and aluminum in containment, running the ECCS spray systems for the proper duration, and adjusting the calculation to reflect the fact that the marinite has been removed from containment results in 70 percent less aluminum, 20 percent less silicon, and 65 percent less calcium than was predicted for a design basis LOCA. Furthermore, applying the quantities of concrete and fiberglass exposed by a LOCA on a 6-inch cold leg break (Case 7) results in a 97 percent reduction in aluminum, 93 percent reduction in silicon, and 96 percent reduction in calcium from the baseline condition. As an addition reduction in debris generation, little or no Microtherm debris is generated for most 6-inch pipe breaks because this insulation material is only present in the bioshield wall penetrations. A pipe break would have to be in the vicinity of a wall penetration to generate any Microtherm debris, and the quantity of Microtherm in any one penetration is minimal. An important cause of the reduced release of chemicals is the change in the temperature profile. The temperature profile of the design basis LOCA is considerably higher than for a MBLOCA, and as an additional conservatism the temperature profile was increased by an additional 5 °F when the corrosion product quantities were calculated for the design basis LOCA [5]. The temperature profile of the original STP calculation and the profile for a MBLOCA are shown in Figure 2.

The quantities of chemicals released into solution during a MBLOCA, based on calculations from the WCAP-16530-NP procedure, are 1.70 kg of Al, 2.36 kg of Ca and 13.16 kg of Si. The concentration of aluminum and calcium in solution and loading rate onto a strainer is summarized in Table 3, along with the corresponding values that were tested at Alden as described in the previous section. As is evident in this table, the concentrations and loading rates for calcium and aluminum in a MBLOCA are substantially lower than the values for a design basis LOCA or the values that were tested at Alden.

The concentrations of aluminum and calcium during a test are significant if the concentrations are near the saturation concentrations of the relevant precipitates. If the concentrations are significantly above the saturation limits, the concentrations will not necessarily affect the total head loss achieved during a head loss test but may affect the rate at which head loss accumulates. The concentrations of aluminum and calcium in the Alden tests were higher than predicted for a design basis LOCA because the water volume in the test system was not scaled to the water volume in the STP containment pool during a LOCA. The water volume in the Alden test was 1830 gal, whereas the water volume that would correspond to the ratio of ECCS screen areas in the STP plant and Alden test would be 16,830 gal. This difference in water volumes resulted in concentrations in solution that were 9.2 times greater and a pool turnover time that was 9.2 times shorter in the Alden tests than would be calculated to be present in a design basis LOCA at the STP. While the difference in concentration may not have a significant difference in total head loss for a design basis LOCA, a longer pool turnover time would have slowed the rate at which precipitates were deposited on the strainer and would have greatly increased the amount of time necessary to conduct the tests.

Table 2 – Summary of quantities of Aluminum, Silicon, and Calcium Released from the STP Plant during a variety of LOCA conditions.

Case	Al (kg)	Si (kg)	Ca (kg)	Description
0	82.92	208.85	63.06	Baseline calculation for a design basis LOCA [5].
1	82.92	184.91	28.58	Same as baseline but eliminates 15.2 ft ³ of calsil insulation from the calculation due to the removal of marinite from the STP containment building. Marinite was originally installed on the reactor vessel nozzles but has been removed.
2	67.54	184.91	28.58	Same as Case 1 but adjusts the aluminum quantity from 7,000 ft ² to 5,567 ft ² to be consistent with the best estimate of the quantity of aluminum in containment [6].
3	25.41	185.07	28.51	Same as Case 2 but adjusts the spray duration to 6.5 hours instead of assuming that the sprays run for the entire 30 day duration.
4	24.56	169.48	23.16	Same as Case 3 but adjusts the pool water volume ^A from 89,350 ft ³ to 73,400 ft ³ , which is the best estimate of the pool water volume during MBLOCAs and LBLOCAs [7].
5	24.56	169.45	23.09	Same as Case 4 but adjusts the quantity of concrete from 5,700 ft ² to 1,446 ft ² , based on the best estimate of exposed concrete in a LBLOCA [8]. Note that the contribution of chemicals from concrete dissolution is minor compared to other materials.
6	19.72	21.76	2.38	Same as Case 5 but adjusts the quantity of Nukon from 2,385.1 ft ³ to 60 ft ³ , based on the best estimate of NUKON fiberglass debris generated in a 6-inch cold-leg break MBLOCA [9].
7	1.70	13.16	2.36	Same as Case 6 but adjusts the pool temperature profile from the base condition to a 6-inch break on a cold-leg pipe [10] and adjusts the pH after TSP addition is complete from 7.49 to 7.20, which is the average pH measured over 30 days in the CHLE MBLOCA test. This case is a prediction of the quantities of materials that would be released into solution due to corrosion and dissolution during a 6-inch cold-leg break MBLOCA at the STP plant using realistic conditions and assumptions.
8	1.70	12.76	2.35	Same as Case 7 but eliminates the concrete (1,446 ft ²) and microtherm (1.8 ft ³). This case is a prediction of the quantities of materials that would be released into solution due to corrosion under the conditions tested in the CHLE test, which did not include concrete and microtherm. The calculated contribution from the concrete is 0.01 kg of Ca and 0.007 kg of Si.

^A Based on density of the containment sump solution at 185 °F, 60.957 lbm/ft³,

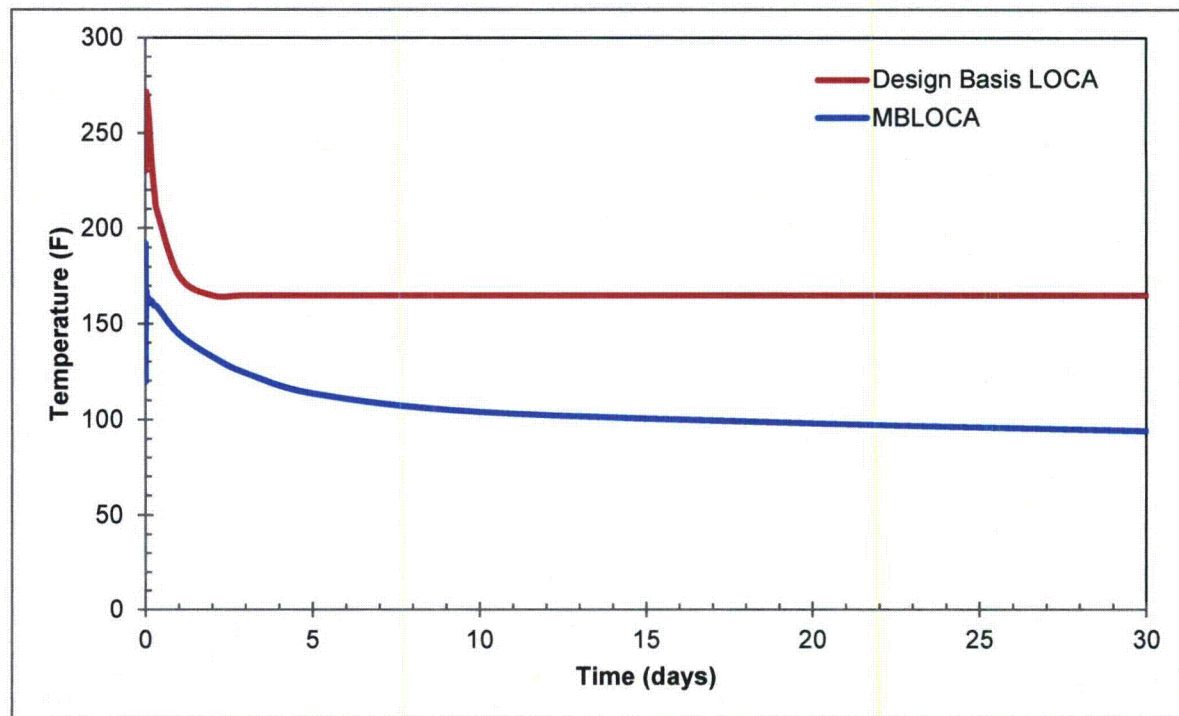


Figure 2 – Temperature profiles of (a) the design basis LOCA used to determine the quantities of precipitates for prototypical strainer testing and (b) a MBLOCA of a 6-inch cold leg break.

The more important factor in head loss testing is the screen loading rate. The screen loading rate in the Alden test was the same as calculated for a design basis LOCA for calcium, but higher than calculated for a design basis LOCA for aluminum. The higher screen loading rate for aluminum resulted from two factors. First, the design condition for the Alden tests used the quantity of $\text{NaAlSi}_3\text{O}_8$ precipitate generated for the maximum water level condition and the AlOOH precipitate generated for the minimum water level condition. The increase of AlOOH precipitate in the minimum water condition is caused by a reduction in the amount of silicon available to form $\text{NaAlSi}_3\text{O}_8$ precipitate, not by an increase in the amount of aluminum available. Thus, the same aluminum in solution contributes to one precipitate in the maximum water condition and the other precipitate in the minimum water condition, but the two precipitate quantities were added together in determining the total amount of aluminum precipitates to use for testing. Second, AlOOH precipitate was used as a substitute for $\text{NaAlSi}_3\text{O}_8$ precipitate (as allowed in the WCAP-16530-NP protocol), but the result of substituting AlOOH for $\text{NaAlSi}_3\text{O}_8$ precipitate on a mass basis increases the total amount of aluminum nitrate that must be added to the system. As given in the recipes in WCAP-16530-NP [1], it is necessary to add 625 g of aluminum nitrate for every 100 g of AlOOH , but only 143 g of aluminum nitrate for every 100 g of $\text{NaAlSi}_3\text{O}_8$. By substituting AlOOH for $\text{NaAlSi}_3\text{O}_8$, the total amount of aluminum that was added to the system was increased.

Table 3 – Concentration and loading rates of aluminum and calcium under design and medium break LOCAs at STP.

	WCAP-16530-NP calculation for MBLOCA at STP	WCAP-16530-NP calculation for design basis LOCA at STP	As tested for design basis LOCA at Alden
Concentration of aluminum added (mg/L as Al)	0.84	32.9	1,220
Loading rate of aluminum on ECCS strainer (g/m ² as Al)	5.0	250	990
Concentration of calcium added (mg/L as Ca)	1.16	24.9	240
Loading rate of calcium on ECCS strainer (g/m ² as Ca)	7.0	190	190

General Experimental Approach for the CHLE Tests

The CHLE program was designed to experimentally evaluate the impact of chemical precipitates on the risk-informed resolution of GSI-191 under realistic conditions at STP. The overall test program was envisioned to include several components, including (1) a limited set of 30-day tests to investigate the overall chemical effect scenario in an integrated fashion under realistic conditions, (2) bench-scale tests to investigate variability in corrosion and release rates as a result of variability in chemical concentrations and other factors during a LOCA, and (3) vertical-column head loss tests to identify the extent of head loss under varying debris bed conditions using precipitates generated in-situ based on information generated during the 30-day tests. A test plan [11] for the experimental program was developed and modified several times as the program evolved, as results were generated, and as additional information became available. Not all components of the test program were completed during 2012. Key tests that were completed included two 30-day tests, which simulated a MBLOCA (6-inch break) and LBLOCA (15-inch break), along with preliminary tests that evaluated the performance of two types of fiberglass debris beds.

The CHLE test equipment for the 30-day tests consists of a material corrosion tank and three vertical head loss modules. The 304 stainless steel tank, as shown on the left in Figure 3, is nominally 4 ft x 4 ft x 6.6 ft and has a bottom that slopes to a centrally-located discharge port. Although the inside of the tank is not physically divided into different compartments, the tank can be visualized as containing upper and lower sections. The upper section of the tank is designed to accommodate all vapor space materials in containment that contribute to chemical effects through exposure to containment sprays. The lower section of the tank is designed to accommodate solution and materials that may be submerged in containment. A removable cover and gantry crane allow for placing and removing samples into the desired areas of the tank. The tank is not pressurized and is therefore limited to testing below the normal boiling point of water.

The tank is insulated and contains two titanium-jacketed 3.5-kW rod-type heaters in the tank pool to maintain the temperature of the solution at a maximum of 185 °F (85 °C) \pm 5 °F. Solution can enter the tank through injection headers in the lower portion of the tank (submerged area) and/or through spray nozzles in the upper portion of the tank (non-submerged area). Additional details of the experimental equipment are described in [12].

The three identical vertical head loss modules, as shown in Figure 4, are designed to operate in parallel when connected to the corrosion tank or individually when isolated from the corrosion tank. Each has an independent pump so that the flow rate to each column and velocity to the screen area can be separately controlled. The nominal velocity through the screen area during testing was 0.01 ft/s. The upper and lower portions of the 6-in diameter vertical head loss modules are constructed of stainless steel and are sealed at the top with a blind flange. The blind flanges can be removed to introduce debris into the head loss assembly. The upper section of piping also has an air vent to allow gas to be vented from the head loss assembly, if necessary. The middle section of the assembly is constructed of 1/4-in thick polycarbonate to allow view of the debris bed (6 inches below and 16 inches above) with a perforated plate supported by a ring located 6-in from the bottom. The perforated plate is constructed of stainless steel and contains 0.094-inch holes in the same pattern as on the STP strainers. There are vents above and below the screen support to assist in post-test activities. A differential pressure (DP) transducer is piped to ports above and below the screen support to measure the pressure loss through the debris bed. Each module has a dedicated flow meter to monitor flow to the column.



Figure 3 – CHLE tank.

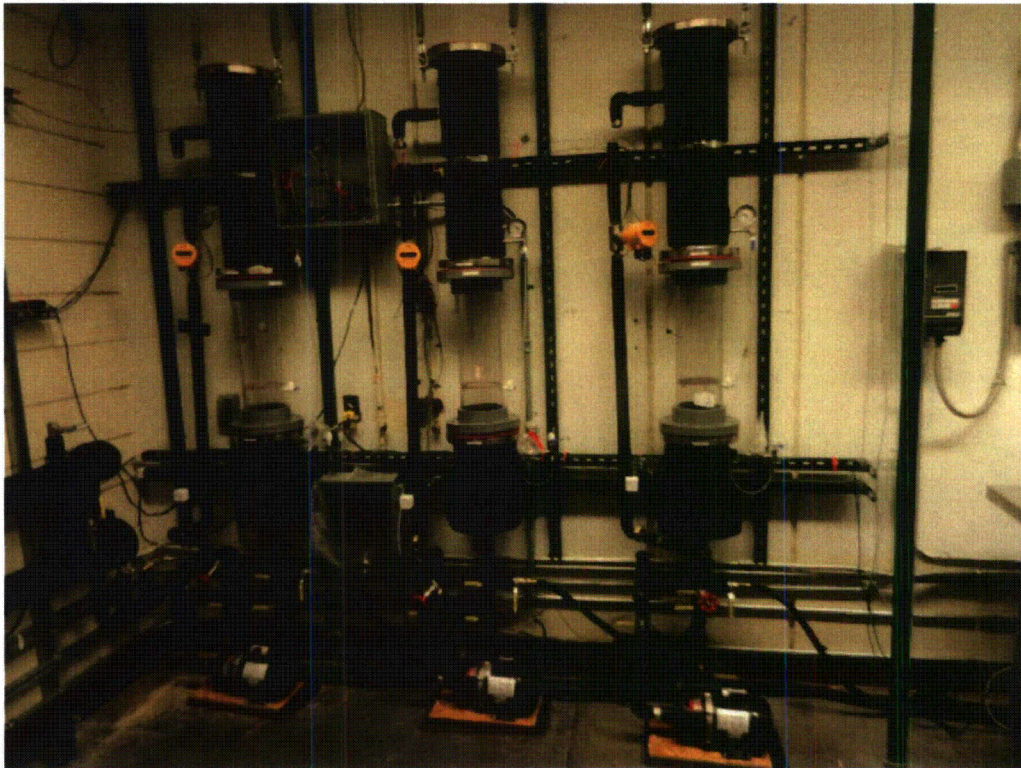


Figure 4 – CHLE Head Loss Columns.

As noted earlier, tests to simulate strainer head loss can be scaled to full-scale installations based either on containment pool volume or on screen area. Head loss testing is appropriately scaled on the basis of screen area so that screen loading rates can be maintained. For the effects of chemistry, however, it is necessary to scale the quantities of materials in the system on the basis of containment pool volume, so that the concentrations of species in solution in the CHLE system would properly simulate the concentrations that would occur in the full-scale installations. Matching concentrations is important because the kinetics and outcome of chemical reactions depends on the concentrations of the reactants present. However, it was also necessary to consider the ratio of screen area to ensure that the CHLE tests did not result in a screen loading rate that was below the rate that would occur in the STP plant. Based on pool volumes, the volume of water in the STP containment during a LOCA is 1,790 times greater than the volume in the CHLE system, and all materials used during testing were scaled to this ratio. However, the screen area in the STP plant when two ECCS trains are in operation is 3,631 ft², compared to 0.59 ft² in the CHLE system with three 6-inch diameter screens, resulting in a ratio of 6,160. Thus, the CHLE system was conservatively designed with less screen area than would be properly scaled to the STP plant to provide a screen loading rate greater than that which would occur with the same quantity of precipitates in the STP plant. The increase in screen loading rate based on the design of the CHLE head loss columns is a factor of 3.4.

An important consideration is that the fiber debris beds that are used in the chemical effect testing be suitable surrogates for debris that would be formed during a LOCA. Attributes that affect the suitability of a particular debris bed design include the stability of the debris bed, the

reproducibility of the results, and the ability of the debris bed to participate in chemical interactions under a variety of conditions. Debris beds used in some previous GSI-191 work are not necessarily applicable to the current study for three reasons. First, the approach velocities historically used in head loss testing were more than an order of magnitude higher than the STP strainer design and testing was often conducted with tap water and at room temperature. Second, the historical observations were typically for short periods compared to the CHLE investigations. Third, the NEI recently developed a debris preparation method [2] that is believed to be prototypical of debris formed during a LOCA, and most previous head loss testing have used other debris preparation methods. The Nuclear Regulatory Commission (NRC) reviewed the NEI plan and noted it is generically an acceptable way of producing debris, but declined to officially endorse it as the only way to produce acceptable debris because of the dependence on human actions [13].

Two types of fiber bed preparation methods were evaluated for possible use within the CHLE program. First, the recent debris formulation advocated by NEI for strainer testing involves baking fiber blankets on one side at 300 °C for 6 to 8 hours, followed by disaggregation with a commercial pressure-washer; this method is referred to as the NEI pressure-washing method in this report. Second, fiber blankets were subjected to the same baking procedure, but were separated by fine chopping of fibers in a blender. The NEI pressure-washed fiber, when introduced into a head loss column, results in a light and fluffy debris bed. The blender-processed fiber results in a denser bed with a more uniform top surface. Photographs of fibers after the two preparation methods are shown in Figure 5, and the respective debris beds are shown in Figure 6. Performance of the debris beds with respect to head loss and the ability to capture precipitates is discussed later in this report.

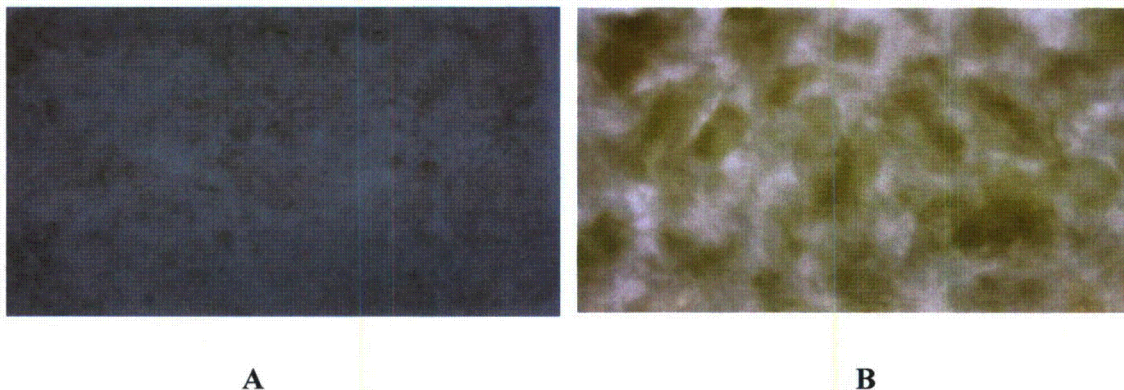


Figure 5 – Examination of debris on a light table from (A) blended fiber preparation, and (B) NEI pressure-washed fiber preparation.

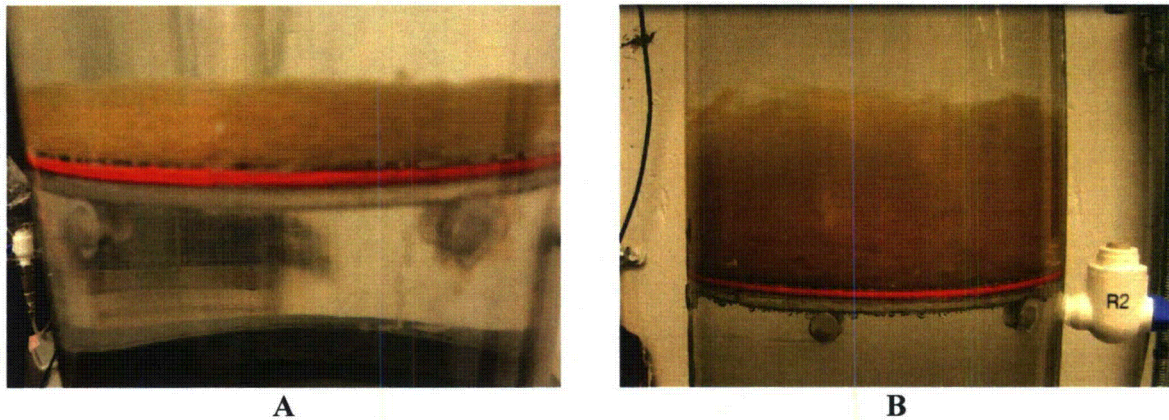


Figure 6 – Debris beds in head loss columns at the beginning of test operation. (A) Column 2 blended fiber debris bed and (B) Column 2 NEI pressure-washed fiber debris bed.

Chemicals concentrations representative of the containment pool at STP during a LOCA were used throughout the testing program. Water was deionized to a conductivity less than 50 $\mu\text{S}/\text{cm}$ using a reverse osmosis system. Chemicals included 250.5 mM boric acid (2,710 mg/L as B), 8.87 mM trisodium phosphate (3,370 mg/L as $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$), and 0.061 mM lithium hydroxide (0.42 mg/L as Li). Hydrochloric and nitric acids were added periodically over the duration of the 30-day tests to simulate acid production from radiolysis, with maximum concentrations of 0.812 mM HCl and 0.229 mM HNO_3 . The basis for the chemical concentrations is described in additional detail in [14].

Corrosion and Precipitation in a Medium Break LOCA in the 30-day CHLE Test

A long-term test was conducted from 22 Aug 2012 to 25 Sept 2012 to simulate the interaction between materials in containment and the containment pool solution during a 6-inch break on a cold-leg pipe in the STP containment building. The test included materials in the corrosion tank and solution that continuously circulated through the tank and through fiberglass debris beds on the screens in the three vertical head loss columns.

The overall duration of the test was 34 days. The NEI pressure-washed debris beds were present in all 3 columns during the first 30-day period and the blender-prepared debris beds were present in all 3 columns for the last 4 days. The NEI pressure-washed debris bed was selected for the 30-day test because the blender-prepared debris beds were not sufficiently reproducible in a previous test series to allow chemical precipitates to be adequately detected (described later in this report). However, preliminary tests also demonstrated that the blender-prepared debris beds were more effective at capturing chemical precipitates circulating in the pool solution, and there were concerns that the NEI pressure-washed debris beds may not be sufficiently sensitive. On Day 30, the columns were isolated from the tank, the NEI debris beds were removed, and blender-processed beds were installed. Fresh TSP-buffered borated solution was circulated

through the blender-processed debris beds (isolated from the solution in the corrosion tank) to establish baseline behavior for 2 days. The columns were then linked to the corrosion tank and the test solution was allowed to circulate through the blender-processed debris beds for an additional 2 days. Thus, if precipitates had been formed and were circulating in the pool solution after 30 days of simulated LOCA duration undetected by the NEI pressure-washed debris beds, the blender-processed debris beds would provide an additional opportunity to detect the presence of precipitates in the pool solution.

During the 30-day test, the head loss columns each contained 18 g of fiberglass debris to maintain consistency with the debris beds from previous tests. The column approach velocity was maintained at 0.01 ft/s. An analysis using Containment Accident Stochastic Analysis (CASA) determined that the appropriate amount of fiberglass debris scaled to the volume of the CHLE pool volume was 36.5 g; thus, the 54 g (total) of fiber present in the columns was about 50 percent greater than the quantity required to realistically simulate a 6-inch break. To maintain the proper ratio of aluminum to silicon for corrosion and dissolution purposes, the portion of the aluminum that was allocated to the submerged portion of the tank was also increased by 50 percent. Thus, while the total amount of aluminum was correctly scaled for a 6-inch break, increasing the fiberglass and the submerged portion of the aluminum provided somewhat conservative test conditions with respect to realistic conditions for a 6-inch break.

The material in the tank consisted of 3.11 ft² of aluminum scaffolding that was obtained from the STP plant, with 15 percent submerged and 85 percent exposed to the containment sprays. The aluminum scaffolding had been in use at the STP plant for a long time and therefore was representative of actual conditions at the STP plant, including being made of the appropriate aluminum alloy and containing any relevant pre-existing scale and surface coatings. About 90 percent of the aluminum in STP's containment is scaffolding. The aluminum scaffolding was washed to try to remove any latent debris or coatings that could become dislodged during the 30-day test and interfere with weight-loss measurements for aluminum corrosion, but without removing any corrosion products that could affect the rate of corrosion.

The test was run using only aluminum and fiberglass so that if precipitates did form, then the characteristics of the precipitates could be compared to precipitates from a previous test in which aluminum nitrate was injected into the tank solution at a slow rate, which is described later in this report.

The temperature profile for the test was determined by running MELCOR and RELAP-5 and was shown previously in Figure 2 [10]. The chemicals in the containment solution were as described in the previous section; the boric acid and lithium hydroxide were added before the test started, the TSP was added over a 65 minute period near the start of the test to simulate the dissolving of TSP in baskets in the containment building, and the hydrochloric and nitric acids were added periodically during the 30 day period. The sprays were operated for 6.5 hours at the beginning of the test. Additional details of the test conditions are available in [15] and complete test results are available in [23].

Corrosion

The rate of aluminum corrosion can be assessed by measuring the weight change of the aluminum specimens before and after the test. The weight of specimens both before and after the test consists of aluminum metal and corroded scale layers. An ASTM standard acid-washing procedure [16] was used to assess the quantity of scale present on the specimens. A complication is that the chemical formula of the scale is not known, so it is therefore not trivial to determine how much of the scale weight is due to aluminum and how much is due to other elements. The aluminum scaffolding provided by STP is non-homogenous with unknown constituents from years of use, which remained after cleaning. The specimens were cut to size for testing, cleaned with mild laboratory soap to remove latent debris, and allowed to dry, as shown in Figure 7. It should be noted that it is not possible to determine whether the pre-test washing procedure removed all latent debris and other materials that may have been washed from the surface and contributed to weight loss during the test. The samples that were to be submerged were from the side of the scaffolding and had a different texture and appearance than the samples cut for the vapor space. Therefore, unused samples taken from locations similar to that shown in Figure 7 (vapor space and submerged samples) were analyzed using X-ray photoelectron spectroscopy (XPS) and scanning electron microscope (SEM) with energy dispersive X-ray spectroscopy (EDX) in efforts to evaluate the original scale composition.

XPS analysis of unused pieces of the pre-test samples detected the presence of multiple chemical species. Interpretation of the analysis determined that two scale types, aluminum phosphate and aluminum oxide/aluminum hydroxide, were present on pre-test samples corresponding to both the vapor space and submerged specimens. Aluminum oxide and aluminum hydroxide have the same binding energy so it is not possible using XPS to tell which species is present. Using the pre-test and post-test information for masses of the aluminum samples, XPS results, and weight measurements of the scale layer that were removed per ASTM standards [16], an experimental aluminum corrosion mass under STP conditions was calculated. The mass was calculated assuming two different scenarios for the composition of the scale, based on the presence of aluminum phosphate in combination with either aluminum oxide or aluminum hydroxide. The weight measurements are summarized in Table 4.

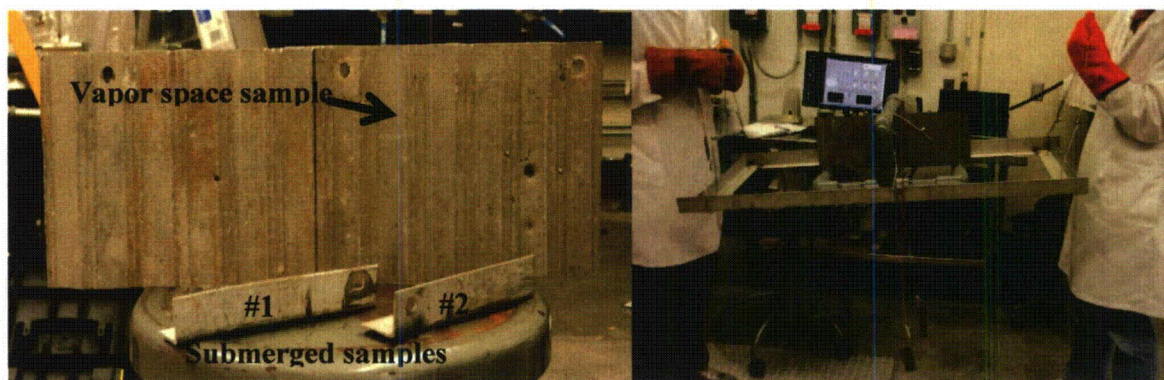


Figure 7 – STP aluminum scaffolding used in this test.

Table 4 – Change in distribution of scales between post- and pre-test sample. Case 1 was calculated assuming aluminum phosphate-aluminum hydroxide scale. Case 2 was calculated assuming an aluminum phosphate-aluminum oxide scale.

Aluminum Sample	Aluminum in Pre-Test Sample			Aluminum in Post-Test Sample			Aluminum mass released to solution		Aluminum converted to scale	
	Al metal (g)	Al in Scale 1 (g)	Al in Scale 2 (g)	Al metal (g)	Al in Scale 1 (g)	Al in Scale 2 (g)	Case 1 (g)	Case 2 (g)	Case 1 (g)	Case 2 (g)
Vapor	834.11	1.41	1.59	833.52	1.61	1.78	0.38	0.40	0.20	0.19
Submerged 1	63.36	0.10	0.13	63.21	0.13	0.17	0.13	0.12	0.03	0.04
Submerged 2	63.72	0.10	0.13	63.56	0.13	0.18	0.13	0.12	0.03	0.04
Total Mass	961.19	1.62	1.86	960.29	1.87	2.21	0.56	0.55	0.26	0.27

Table 5 – Summary of measured aluminum weight loss

	Aluminum metal weight loss over 30 days			
	Calculated in CHLE (g/m ²)	Measured in ICET #2 (g/m ²)	Calculated using WCAP procedure for MBLOCA (g/m ²)	Calculated using WCAP procedure for design basis LOCA (g/m ²)
Submerged	7.1	4.8	18	245
Exposed to spray	2.4	N/A	1.4	103

The total aluminum metal loss due to corrosion was calculated to be 0.59 g as Al from the specimens exposed to containment spray and 0.31 g as Al from the submerged specimens. The aluminum metal lost as a function of surface area is summarized in Table 5. For comparison, corresponding values from ICET Test #2 and WCAP calculations are also shown in Table 5. The submerged specimens in the CHLE MBLOCA test had somewhat more aluminum weight loss than in ICET Test #2 [17]. However, considering that the ICET test used fresh aluminum coupons of a known alloy rather than old scaffolding, was conducted at a constant temperature of 140 °F for 30 days, and did not include a scale removal procedure during the corrosion weight loss measurements, the difference in corrosion rate is not dramatic. The submerged coupons in the CHLE and ICET tests has a lower rate of corrosion than predicted for a MBLOCA by the WCAP calculation, indicating that a small amount of passivation or inhibition of the aluminum surface may be operative.

The specimen exposed to spray in the CHLE test had a somewhat higher corrosion rate than calculated by the WCAP protocol for a MBLOCA, but several factors may have contributed to low accuracy on the vapor specimen calculations. First, it was not possible to execute the acid-

washing procedure on a specimen of the size of the vapor space specimens, so the procedure was performed on a small piece and the percent weight loss due to scale removal was assumed to be the same for the entire vapor space specimen, even though the corrosion products present on the scaffolding clearly were not homogeneous. Second, the measured differences in weight due to corrosion and due to scale removal were very small so that relative errors in measurements could be significant. Third, other materials (latent debris) may have been present on the specimen and subsequently washed off during the spray period, which would have been measured as a weight loss due to aluminum corrosion even though it would in fact have been due to other materials. Because of these factors, the difference in the corrosion rates for the aluminum exposed to spray is not considered significant.

A significant outcome of this analysis is the measured rates in the CHLE are less than 3 percent of the expected corrosion rates in a design basis LOCA, indicating that considerably less aluminum would be available to contribute to potential chemical precipitates.

Concentration of Metals in Solution and Evidence for Precipitation

Several parameters were measured to determine whether precipitates formed in solution. First, turbidity of the pool water was measured on a daily basis. The trend over the course of the test is shown in Figure 8. The turbidity was the highest, ~0.6 NTU, on the first day of testing and gradually decreased over the thirty days of testing. This trend is similar to tests that did not contain corrosion specimens in the tank. The turbidity increased when the blender-prepared debris beds were linked to the tank on Day 32 of the test, likely due to fiber shedding from the new debris beds. Previous testing showed a good correlation between turbidity and aluminum hydroxide precipitates, as shown in Figure 9. The lack of increase in turbidity over the test suggests that precipitates did not form in the solution.

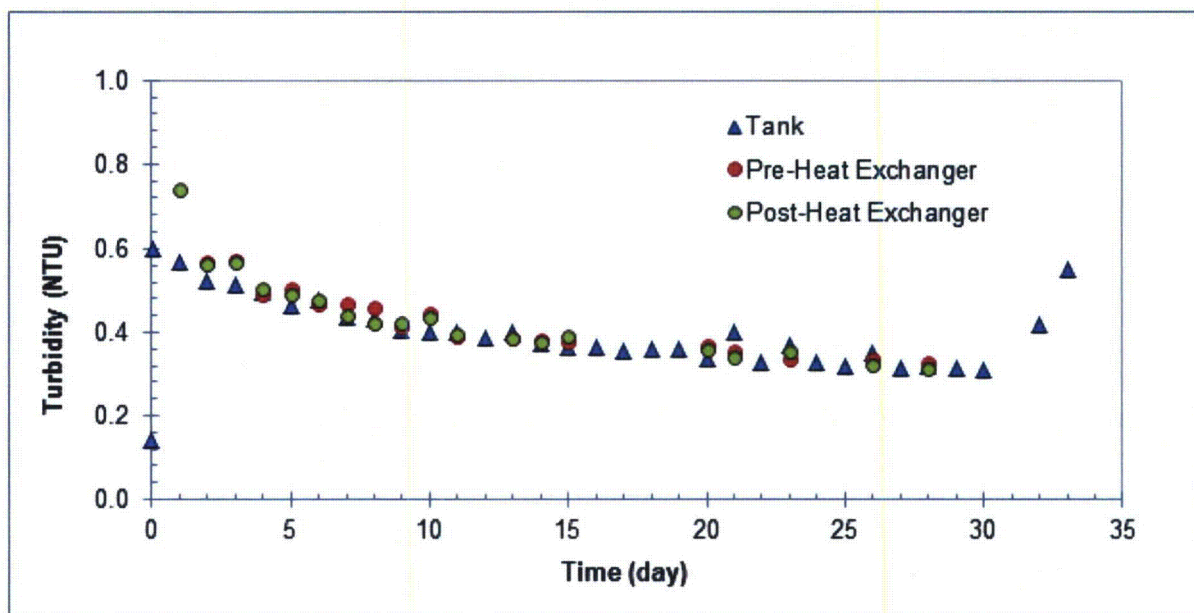


Figure 8 – Turbidity over the duration of the 30-day MBLOCA CHLE test.

A second indicator of precipitation is the difference between filtered and total concentrations of aluminum, silicon, and calcium. The concentrations in solution are measured by inductively coupled plasma optical emission spectrometry (ICP-OES), with and without filtration through membrane filters with a nominal pore size of 0.45 μm . The concentrations over the test are shown in Figures 10, 11, and 12, respectively. The similarity between filtered and total concentrations suggests that no precipitates larger than 0.45 μm in diameter were circulating in solution.

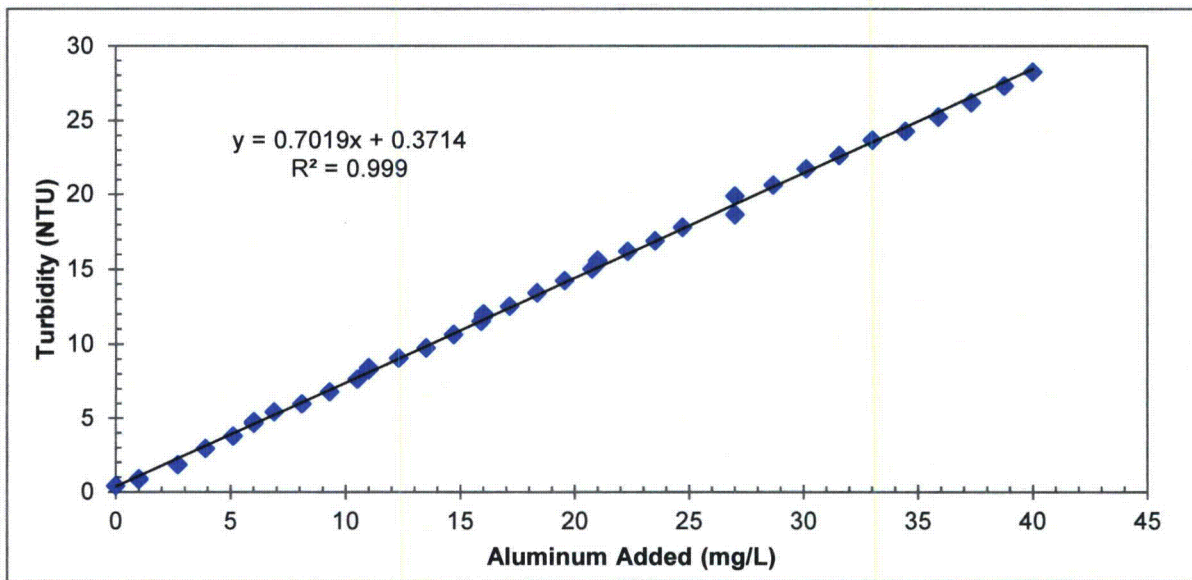


Figure 9 – Correlation between measured turbidity in solution and amount of aluminum added to the CHLE tank in the form of aluminum nitrate.

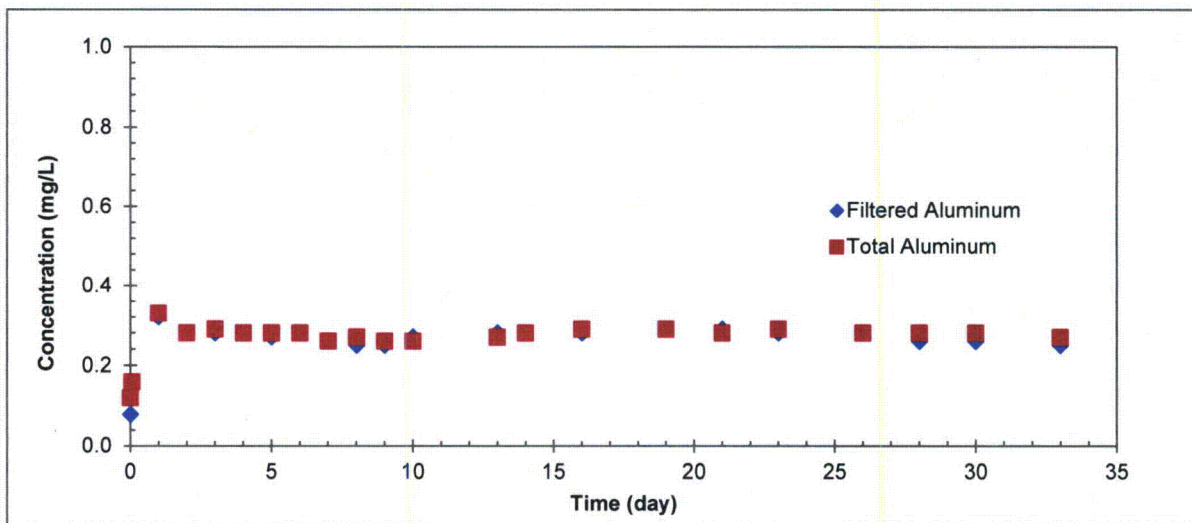


Figure 10 – Total and filtered concentration of aluminum over the duration of the 30-day MBLOCA CHLE test.

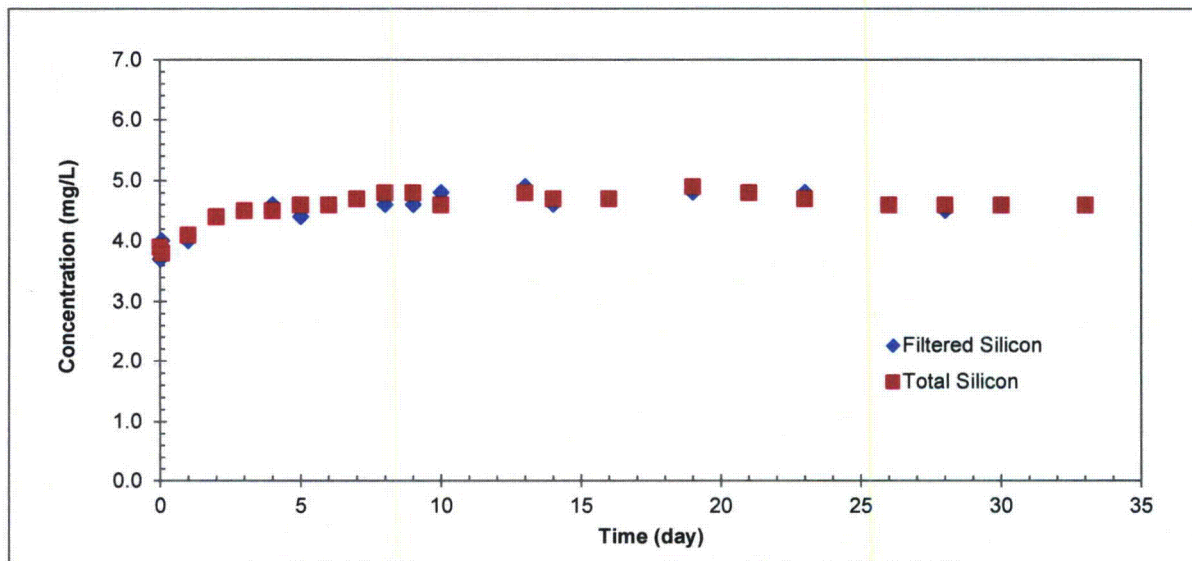


Figure 11 – Total and filtered concentration of silicon over the duration of the 30-day MBLOCA CHLE test.

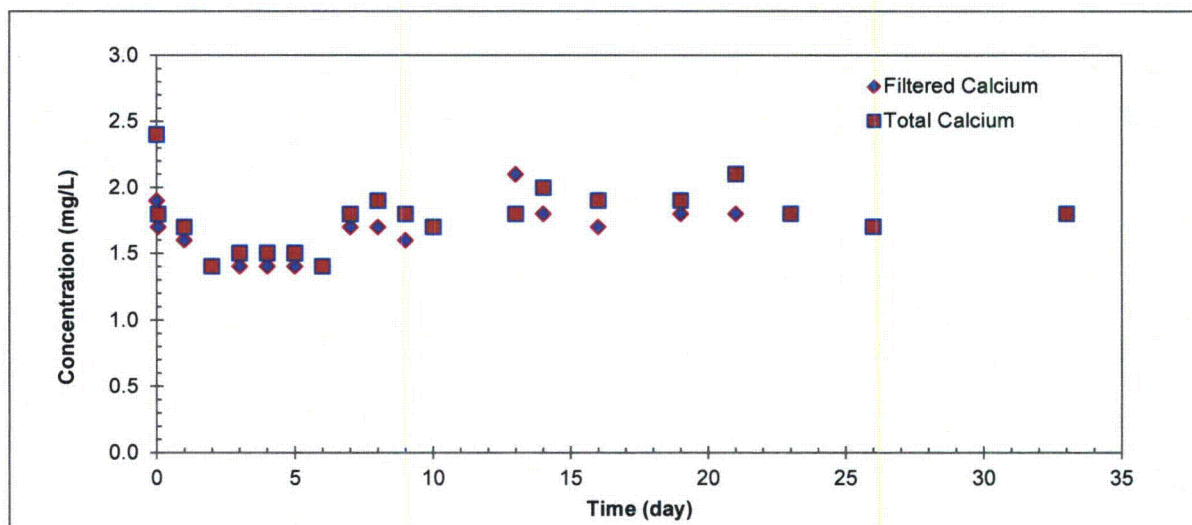


Figure 12 – Total and filtered concentration of calcium over the duration of the 30-day MBLOCA CHLE test.

In each case, the concentration became relatively constant after a few days of testing. The average concentration of each species over the last 20 days of the test is summarized in Table 6. For comparison, the concentration predicted by the WCAP calculation procedure for a MBLOCA are also presented in Table 6. The concentrations of aluminum and silicon are somewhat lower than predicted by the WCAP corrosion rate calculation procedure, and the

calcium concentration is marginally higher. In all cases, however, the measured concentrations are not dramatically different from the concentrations predicted by the WCAP corrosion rate calculation procedure.

The lack of precipitation products can be assessed by comparing the concentrations measured in solution to the saturation concentration of the relevant precipitates. Work conducted at Argonne National Laboratory (ANL), reproduced in Figure 13, suggests that the precipitation boundary for amorphous aluminum hydroxide is a good indicator of the ability of precipitates to form in past GSI-191 head loss testing. Using Visual MINTEQ [18], the precipitation boundaries for aluminum hydroxide and calcium phosphate as a function of temperature and pH are shown in Figures 14 through 17. Figures 14 and 15 show the concentration of soluble aluminum in a solution that is in equilibrium with amorphous $\text{Al}(\text{OH})_3$ solid, and Figures 16 and 17 show the concentration of soluble calcium in a solution that is in equilibrium with amorphous $\text{Ca}_3(\text{PO}_4)_2$ solid (included in the Visual MINTEQ database as species $\text{Ca}_3(\text{PO}_4)_2$ am-2). The saturation concentrations were calculated for initial conditions of 250.5 mM H_3BO_3 , 8.87 mM PO_4^{3-} , 26.61 mM Na^+ , 0.061 mM Li^+ , 0.334 mM Cl^- , and 0.812 M NO_3^- to reflect the chemicals that were added in the MBLOCA test. The figures demonstrate that the concentrations measured in the CHLE tests were below calculated saturation concentrations for these precipitates, except when calcium phosphate was above 70 °C at pH = 7.2, which was the measured pH in the MBLOCA tests. The corresponding value of the 'pH + p[Al]_T' value in the CHLE MBLOCA is 12.2 and is also shown on Figure 13.

Although equilibrium speciation models such as Visual MINTEQ can be helpful in understanding solution behavior, it should be noted that the chemistry of the containment pool solution during a LOCA is extremely complex. The concentrations of the relative species depends on the presence of other species in solution (boron, sodium, etc.), pH, temperature, ionic strength, and a host of other factors including nonidealities, and that many of these factors interact with each other. Thus, thermodynamic modeling can be used as a general indication of the state of a chemical system under specified conditions, but should be used cautiously and should not be construed as being an absolute indicator of the concentrations that would cause certain species to precipitate. Nevertheless, the thermodynamic modeling predictions are generally supportive of the results obtained in this test.

Table 6 – Summary of measured and calculated concentration in a MBLOCA at STP.

	Measured in 30-day MBLOCA CHLE test (mg/L)	Calculated using the WCAP procedure for a 6-inch cold leg MBLOCA, assuming all dissolution materials enter solution (mg/L)
Aluminum	0.28	0.82
Calcium	1.8	1.13
Silicon	4.7	6.14

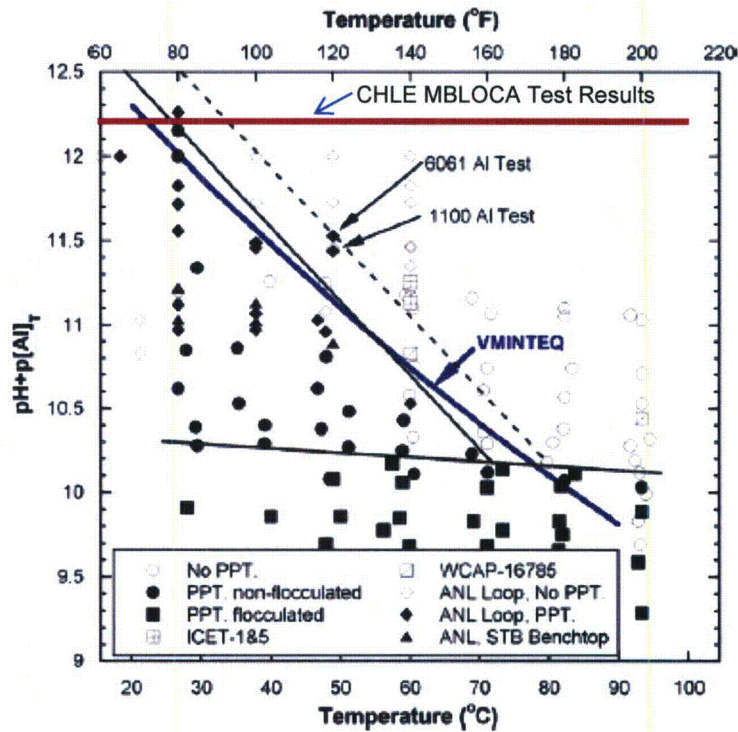


Figure 13 – “Al hydroxide precipitation map in the ‘pH + p[Al]_T’ vs. temperature domain based on ANL’s bench top and loop test data and literature data.” Reproduced from Bahn, et al., 2011 [19]. The red line shows the pH + p[Al]_T value corresponding to the results from the CHLE MBLOCA test.

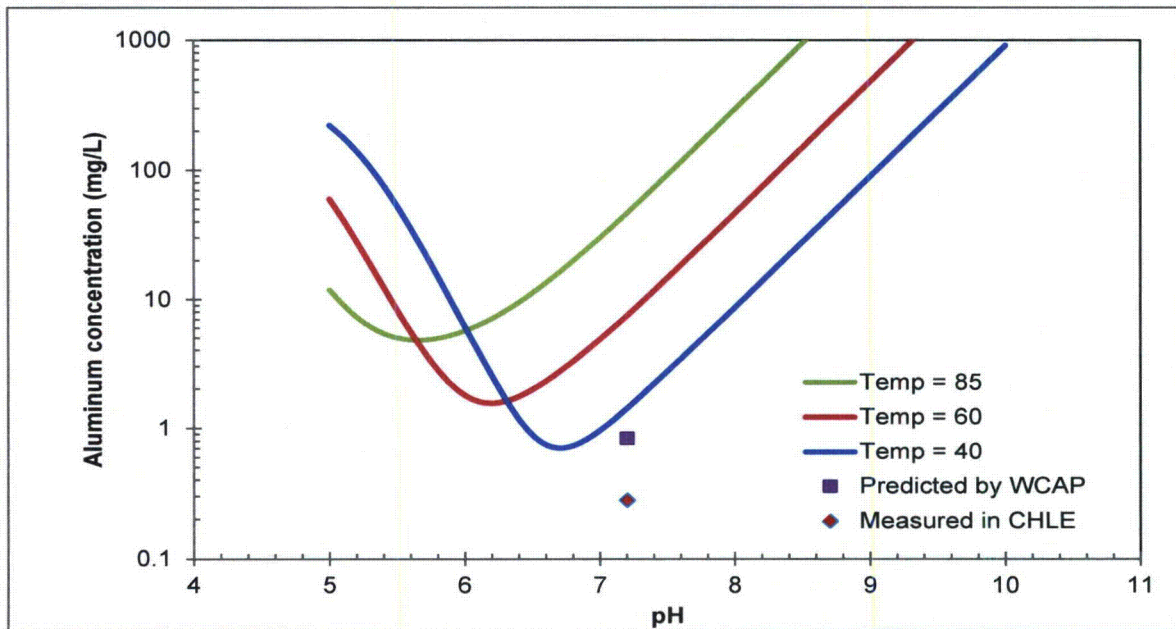


Figure 14 – Equilibrium saturation concentration of aluminum for the formation of amorphous aluminum hydroxide $[Al(OH)_3]$ as a function of pH. Values given for WCAP and CHLE are the concentrations in solution at the end of a 30-day event as a result of corrosion.

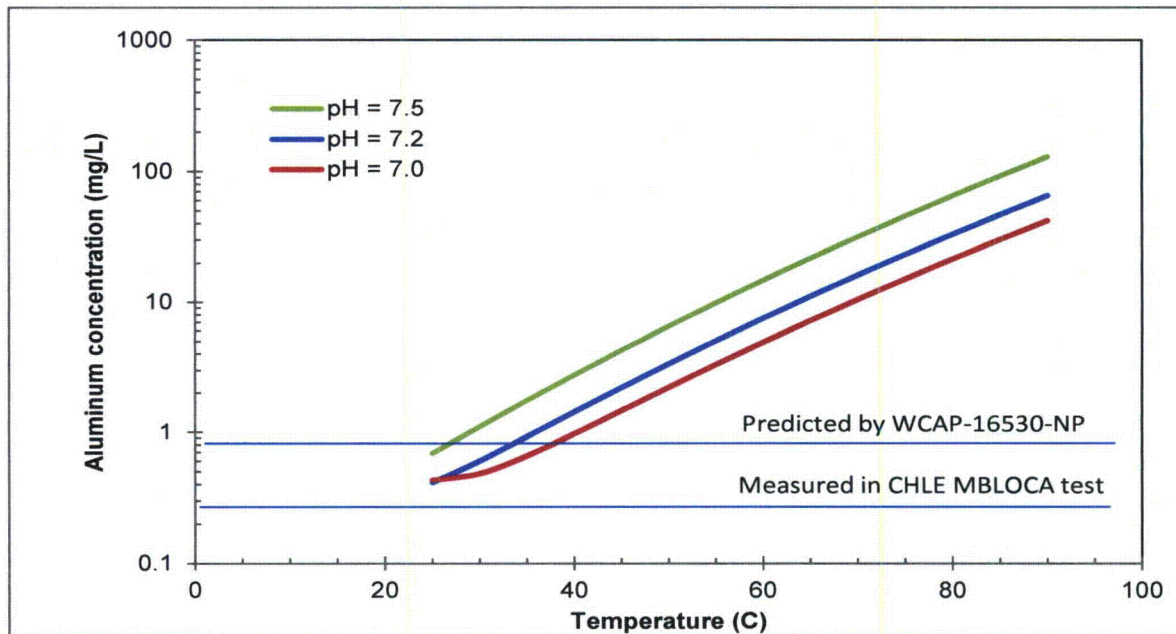


Figure 15 – Equilibrium saturation concentration of aluminum for the formation of amorphous aluminum hydroxide $[Al(OH)_3]$ as a function of temperature. Values given for WCAP and CHLE are the concentrations in solution at the end of a 30-day event as a result of corrosion (temperature varies during the event).

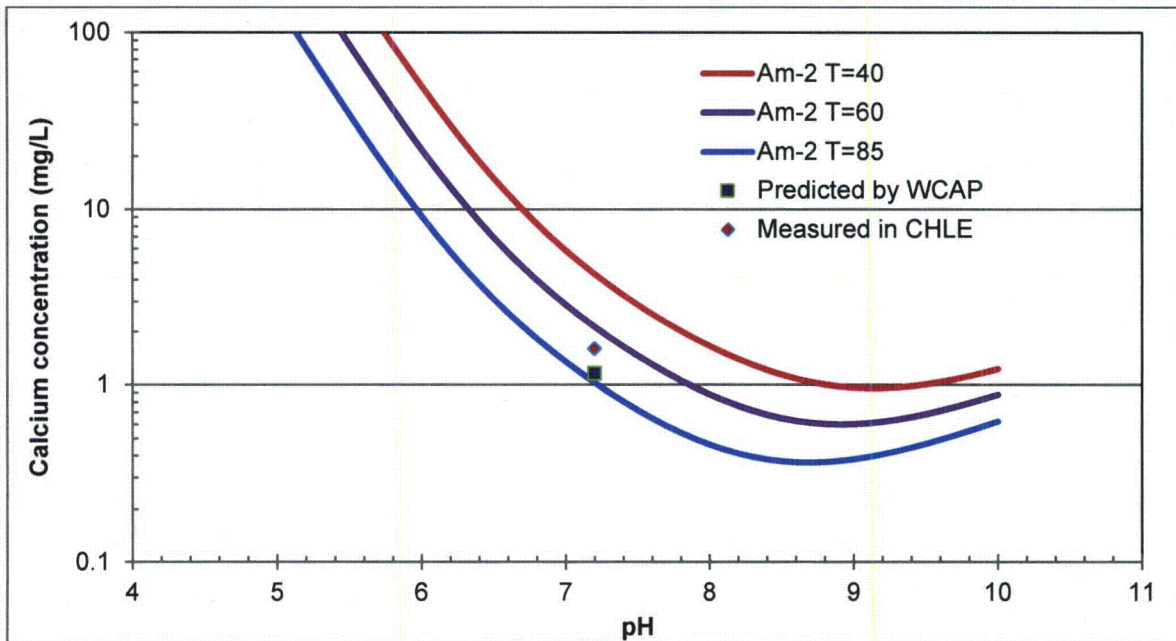


Figure 16 – Equilibrium saturation concentration of calcium for the formation of calcium phosphate $[\text{Ca}_3(\text{PO}_4)_2]$ as a function of pH. Values given for WCAP and CHLE are the concentrations in solution at the end of a 30-day event as a result of corrosion.

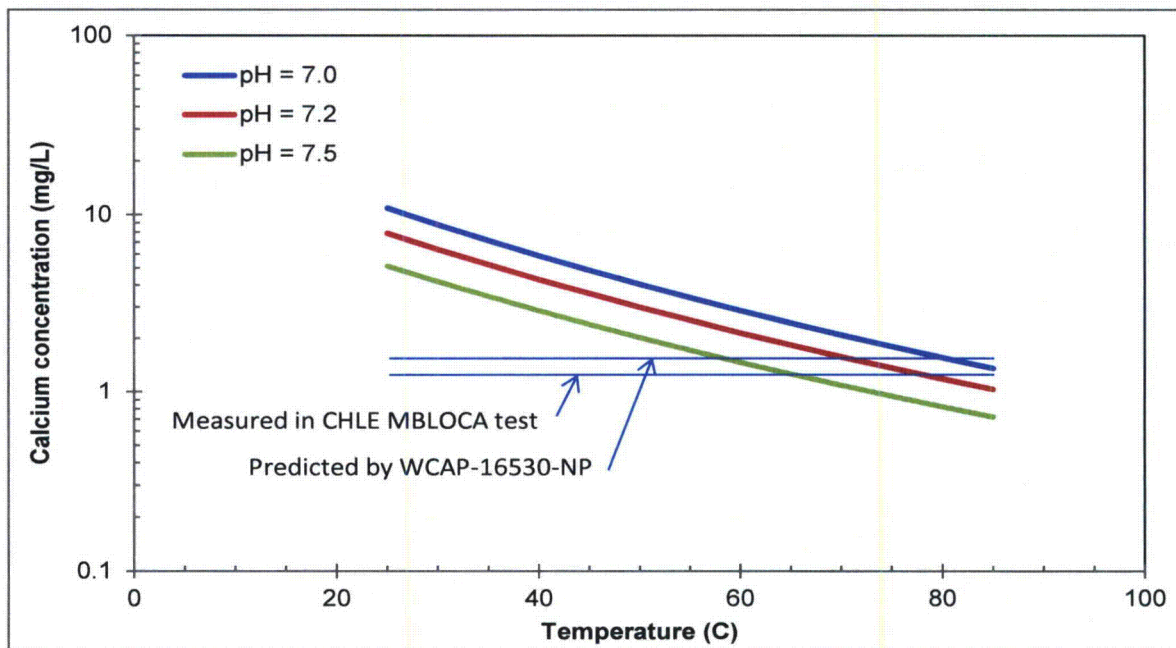


Figure 17 – Equilibrium saturation concentration of calcium for the formation of calcium phosphate $[\text{Ca}_3(\text{PO}_4)_2]$ as a function of temperature. Values given for WCAP and CHLE are the concentrations in solution at the end of a 30-day event as a result of corrosion (temperature varies during the event).

Head Loss

The head loss through the debris beds over the 30-day test is shown in Figure 18. Head loss was normalized to a temperature of 20 °C using corrections for both the density and viscosity of water. The normalized head loss was less than 1 inch over the duration of the test, and did not increase during the 30-day period. As will be discussed later in this report, however, the NEI pressure-washed beds would be unlikely to detect precipitates at the concentration that occurred in this test.

The ability for the available aluminum to cause head loss in a debris bed can be assessed by comparing the results of this test to previous head loss testing. Based on the measured aluminum concentration of 0.28 mg/L, the maximum loading that would occur on the CHLE strainers would be 5.8 g/m² as Al. As noted earlier, the CHLE strainers were designed with less surface area than would be proportional to the STP plant to ensure a conservative loading rate. If the corresponding concentration were applied to the STP strainers, the loading rate would 1.7 g/m² as Al.

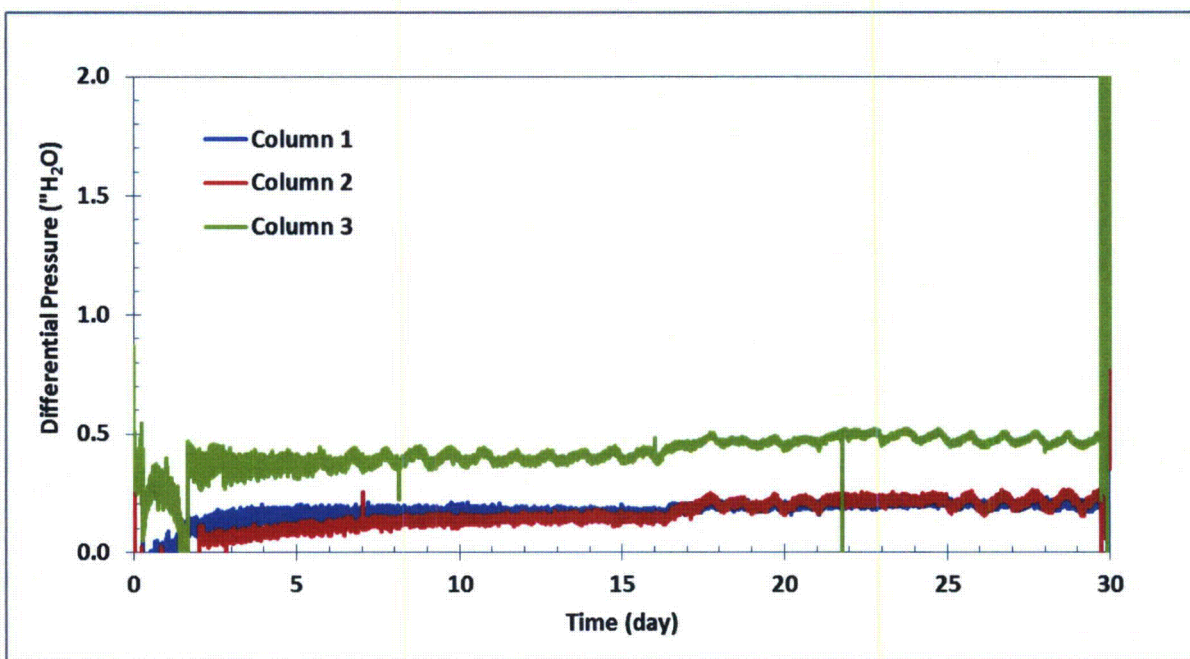


Figure 18 –Normalized head loss through NEI pressure-washed debris beds during the 30-day MBLOCA CHLE test.

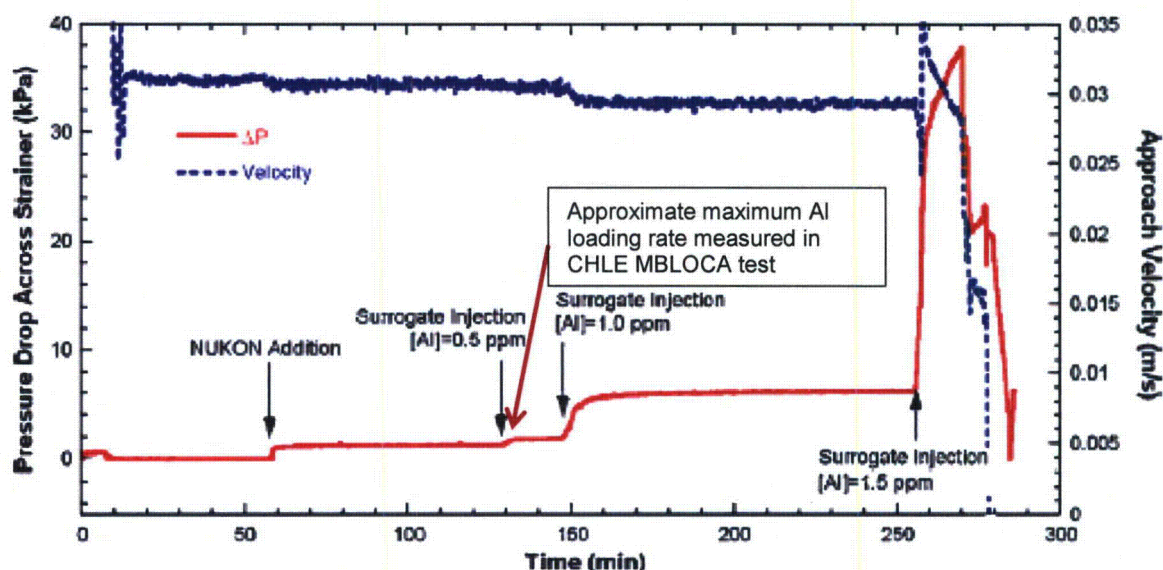


Figure 19 – “Pressure drop and screen approach velocity versus time history in a loop test using the WCAP aluminum hydroxide surrogates” reproduced from Bahn et al, 2009 [20]. The quantity marked with the arrow represents approximately the maximum loading rate that can be achieved in a MBLOCA at the STP plant, using either the measured corrosion quantities in the CHLE test or the calculated corrosion quantities in the WCAP protocol.

This loading rate can be put in context by comparing it to tests conducted at ANL. Results from the ANL testing are reproduced in Figure 19. The point on the graph labeled as 0.5 ppm corresponds to a loading rate of 4.4 g/m^2 as Al based on the surface area of the screens in the ANL test loop. Rapid head loss did not occur until the loading rate reached 13.3 g/m^2 as Al. Similarly, in small-scale chemical effect testing described in NUREG/CR-6868, additional head loss due to chemical precipitates did not begin to occur until the aluminum concentration was 2.7 mg/L and the loading rate was 3.5 g/m^2 as Al [22]. Thus, the loading rate, even if all aluminum measured in the CHLE MBLOCA test were to have precipitated, would be below the quantities that were necessary to cause significant head loss in the ANL testing. The fiber for the ANL debris beds was prepared by coarse shredding, followed by blending in a household blender on high-ice crush mode for 11 seconds, followed by mixing in a beaker with a magnetic stirrer for 10 minutes.

The loading rates can also be compared to strainer module testing conducted at Alden described earlier in this report. The total loading rates during the Alden testing were substantially higher than those described here, reaching a maximum aluminum loading rate of 990 g/m^2 as Al. However, it is also important to note that a significant increase in head loss was observed in the Alden testing as soon as the first batch of aluminum precipitates was added, suggesting that small amounts of precipitate (compared to the total amount) can cause significant head loss. The loading rate for the first batch of aluminum precipitates in the Alden testing, however, was 77 g/m^2 . Since the loading rate for the first precipitate batch was higher than that which caused

rapid head loss in the ANL tests, an increase in head loss in the first batch in Alden test is consistent with the other results reported here. The amount of aluminum released in the CHLE MBLOCA test corresponds to less than one-tenth of the loading of the first batch of aluminum precipitates in the Alden test, so the Alden strainer module testing cannot be used to predict the amount of head loss that may occur under MBLOCA conditions.

Corrosion and Precipitation in a Large Break LOCA in the 30-day CHLE Test

A second 30-day test was conducted from 5 Oct 2012 to 8 Nov 2012. This test simulated a large break LOCA (a 15-inch pipe break, which could be considered an intermediate-sized LBLOCA) under conditions that are representative of the STP plant. Like the previous long-term test, the test was conducted for 34 days, with the NEI pressure-washed debris beds in the three head loss columns for the first 30 days and the blender-prepared debris beds in the columns for the last 4 days. Complete results are available in [24].

In addition to the materials present in the medium break LOCA, this test included a concrete specimen, galvanized steel coupons, and zinc granules that simulated failed inorganic coatings. The test also included a greater amount of fiber debris and a different temperature profile based on predictions for a break of this size.

The temperature profile used for the test is shown in Figure 20. The temperature profile included a higher peak temperature than the MBLOCA test (219 °F versus 193 °F), but the time above the test equipment maximum temperature of 185 °F was only 1.3 minutes. Because of this short duration, the additional corrosion that could occur at temperatures above the maximum test temperature was accommodated by operating the CHLE system at above the LBLOCA profile for a sufficient period of time to cause additional corrosion.

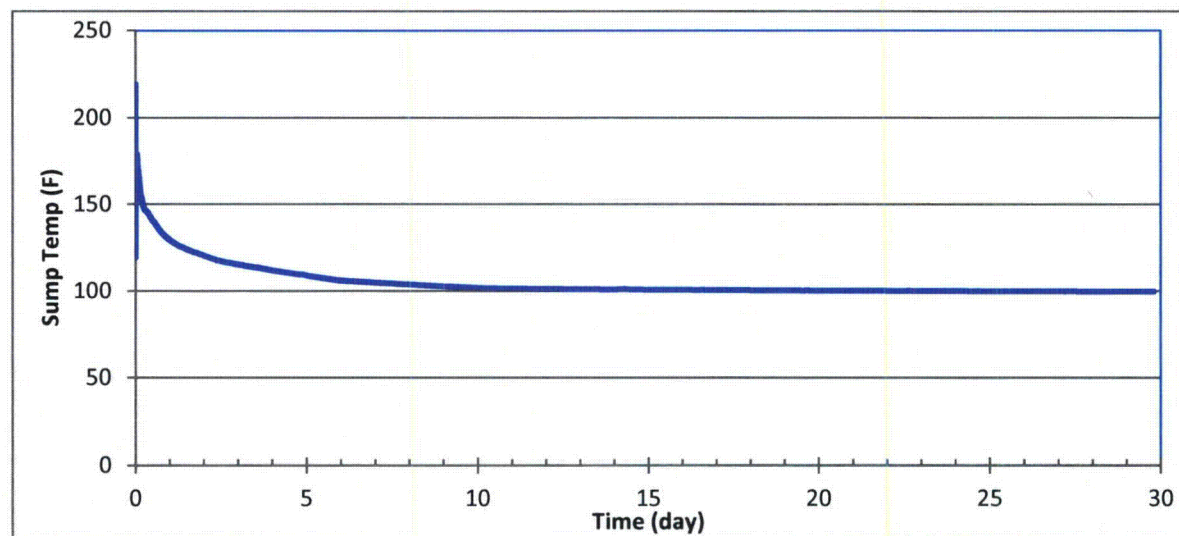


Figure 20 – temperature profile for the CHLE LBLOCA Test.

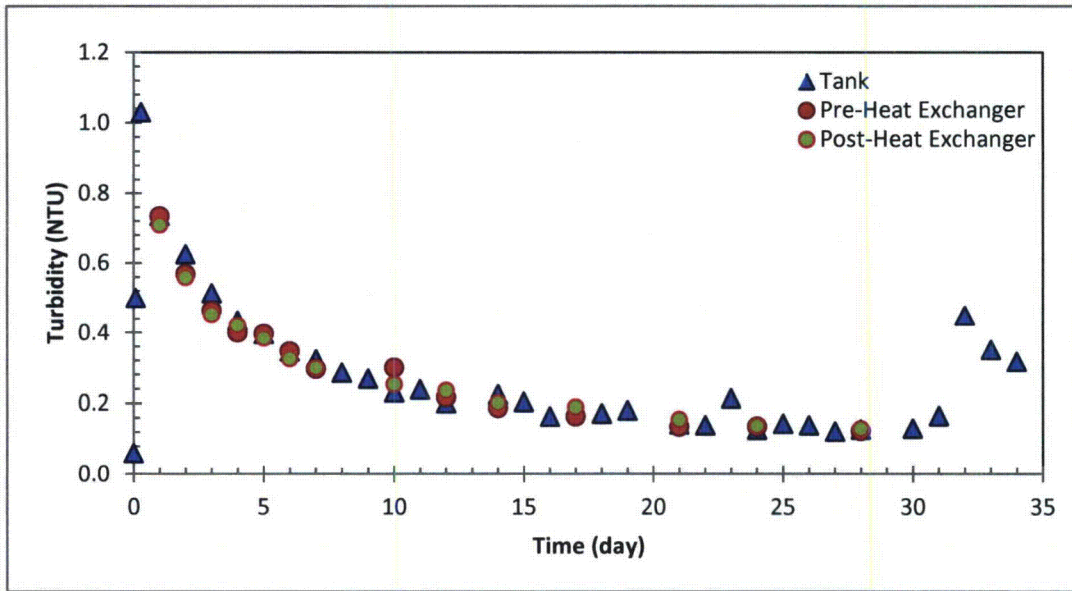


Figure 21 – Turbidity over the duration of the 30-day LBLOCA CHLE test.

The turbidity results from the LBLOCA test are shown in Figure 21. The turbidity follows the same general trend as that which was observed in the MBLOCA test; in this test, turbidity peaked just above 1 NTU after the spray phase was complete and declined to near 0.13 NTU near the end of the 30-day period. The higher turbidity at the beginning of the test was likely due to the additional latent debris introduced into the tank because of the inclusion of additional materials present in the tank. The lack of increase in turbidity over the test suggests that precipitates did not form in the solution.

The total and filtered concentrations of aluminum, calcium, silicon, and zinc over the test are shown in Figures 22 to 25. In each case, the total and filtered concentration for each constituent are similar to each other, which suggests that no precipitates larger than 0.45 μm in diameter were circulating in solution. Throughout the LBLCOA test, the aluminum concentration was lower than in the MBLOCA test, with a concentration that exceeded 0.1 mg/L in only one sample near the beginning of the test. It should be noted that these results are below the quantification limit for these analyses (which is 0.2 mg/L), so it would not be appropriate to infer trends of increasing or decreasing concentration over the duration of the test based on these results. The calcium concentration was around 1.7 mg/L, which is similar to the results obtained in the MBLOCA test. The similarity of the calcium concentration between the two tests is consistent with information that indicates that the leaching from concrete is a small source of calcium compared to other materials in containment (cal sil and fiberglass). The maximum silicon concentration in the LBLOCA test was 2.7 mg/L, which, like aluminum, is lower than in the MBLOCA test. Finally, the zinc concentration increased over the first 10 days of the test and then remained relatively constant at 0.6 mg/L for the duration of the test.

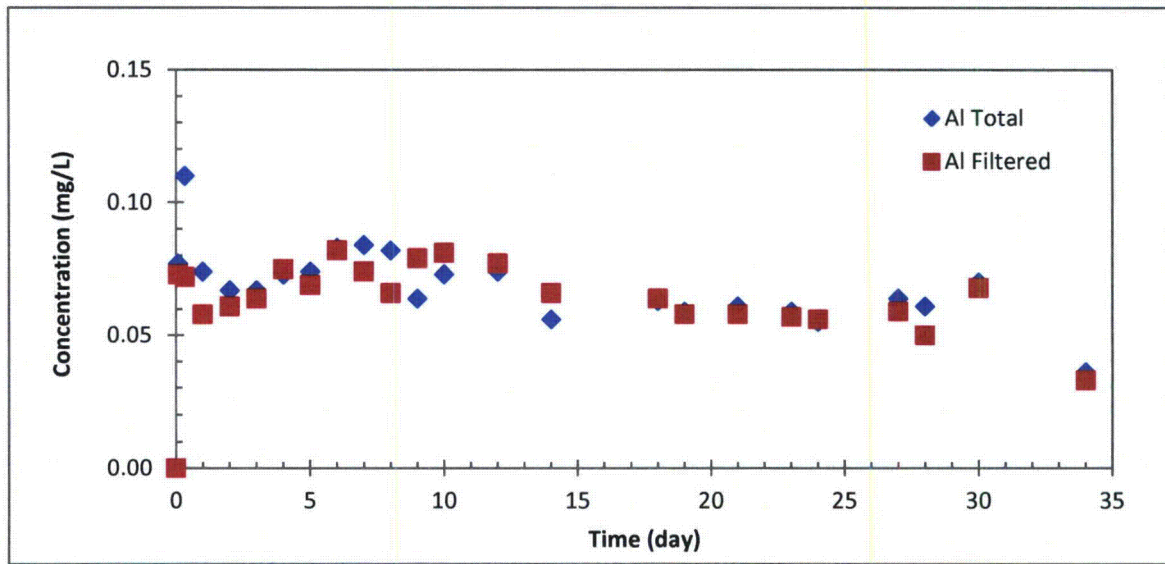


Figure 22 – Total and filtered concentration of aluminum over the duration of the 30-day LBLOCA CHLE test.

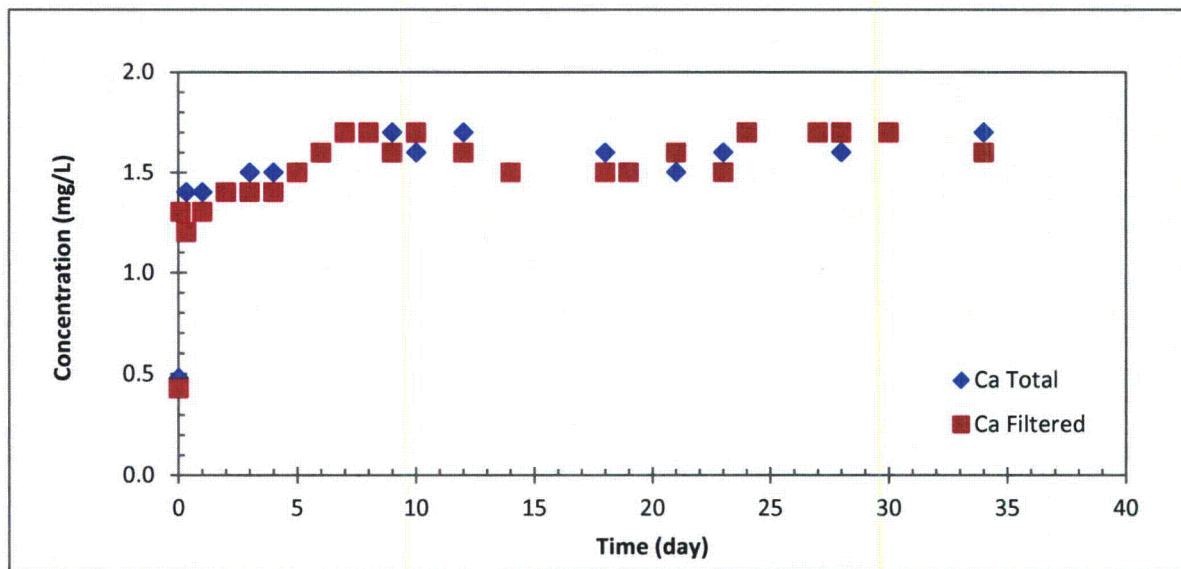


Figure 23 – Total and filtered concentration of calcium over the duration of the 30-day LBLOCA CHLE test.

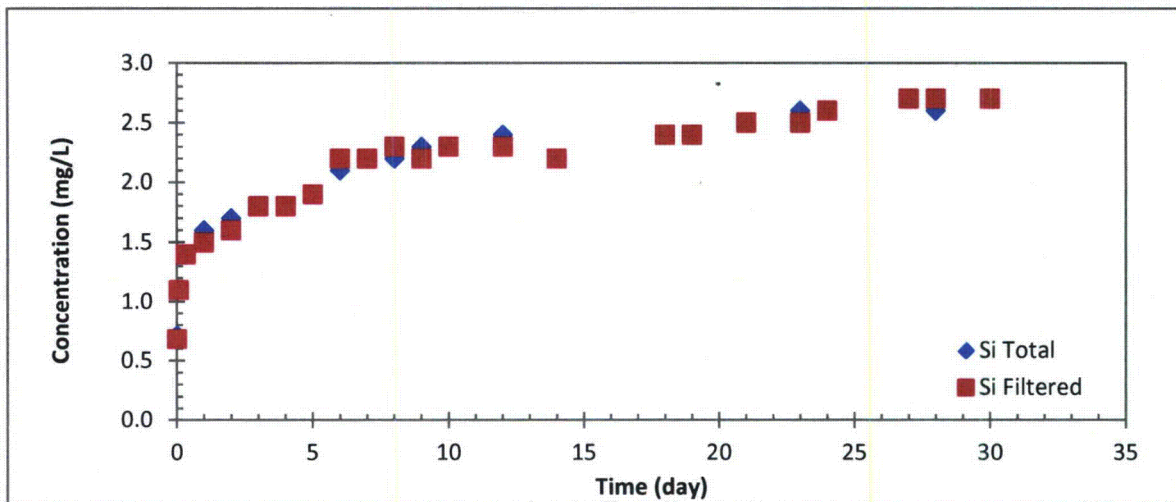


Figure 24 – Total and filtered concentration of silicon over the duration of the 30-day LBLOCA CHLE test.

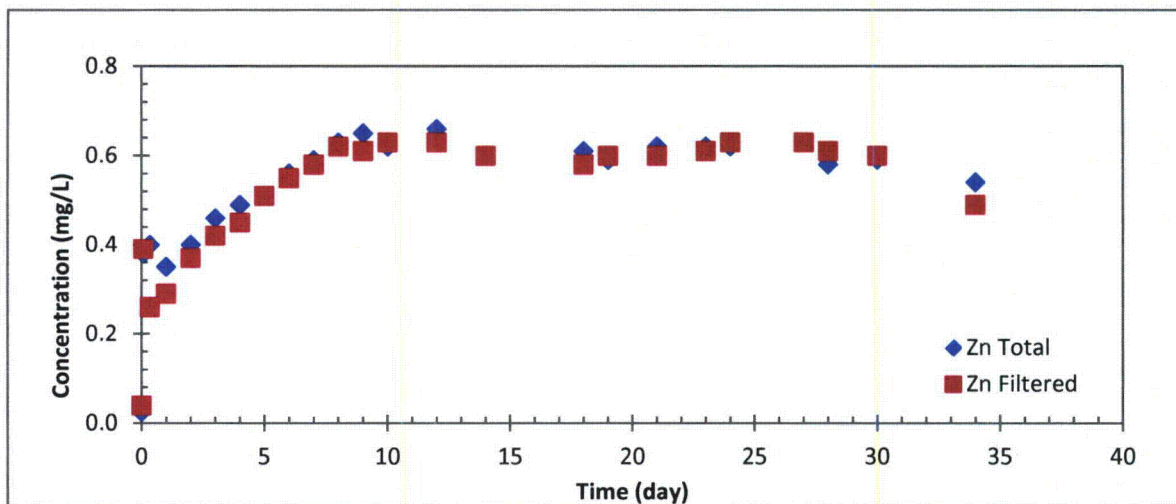


Figure 25 – Total and filtered concentration of zinc over the duration of the 30-day LBLOCA CHLE test.

In contrast to the MBLOCA test, an increase in head loss was observed in the LBLOCA test. The increase in head loss was similar in magnitude for both the NEI pressure-washed debris beds and the blender-processed debris beds. The head loss trend for the NEI pressure-washed debris beds is shown in Figure 26. All columns experienced an increase of head loss; Column 2 had the largest final head loss final value of ~2.5 inches of water, while Column 1 had the smallest head loss value of 0.4 inches of water. Column 3 had a final head loss measurement of 1.2 inches of water. The increase in head loss in the blender-processed debris beds over a 2-day period, as shown in Figure 27, was similar to the increase in head loss during the first 2 days of operation

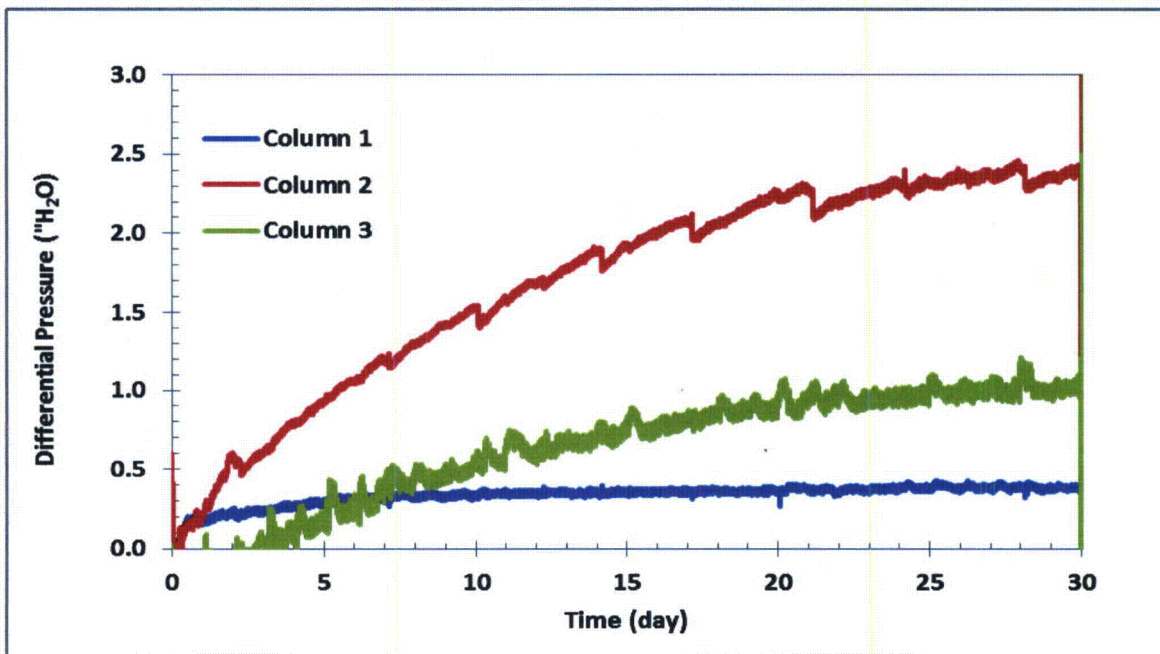


Figure 26 – Normalized head loss through NEI pressure-washed debris beds during the 30-day LBLOCA CHLE test.

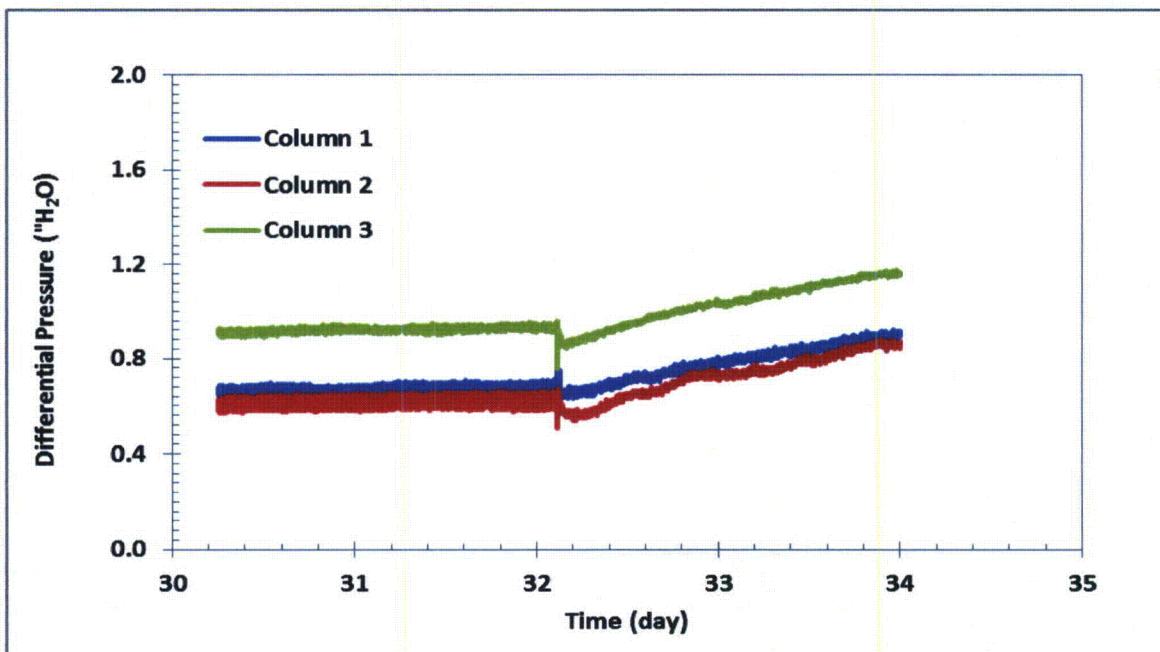


Figure 27 – Normalized head loss through blender-prepared debris beds during the 4-day period at the end of the LBLOCA CHLE test.

of the NEI pressure-washed debris beds. The base-line head loss measurements of all blender-processed debris beds experienced little to no change during the 2 days of isolation (shown as the time between 30 and 32 days in Figure 27), suggesting that a constituent in the water in the tank was responsible of causing the increase in head loss. For both types of beds, however, the overall increase in head loss was small, measuring in just inches of head loss at the end of the testing.

The constituents that contributed to the increase in head loss cannot be identified with certainty. One possibility is the zinc granules that were used to simulate the failed inorganic zinc coatings. The zinc granules were enclosed in a stainless steel mesh bag with the intention of allowing water to circulate through the zinc material without allowing the zinc to circulate through the system, which could contribute to head loss. However, some of the zinc granules did escape from the mesh bag and were evidently circulating with the tank solution, as evidenced by observation of zinc granules on in-line filters that were used to filter solution from the tank periodically, as shown in Figure 28.

Zinc corrosion products were observed upon the conclusion of the LBLOCA test. White materials were observed on discrete areas of the submerged galvanized steel coupons, as shown in Figure 29-A. Similar materials were observed on the tank floor immediately below the submerged galvanized steel coupons. After testing, a similar material was also observed on small areas of the mesh enveloped which contained the zinc granules and the zinc granules themselves. This material was not visibly evident on the fiber debris beds. It should be noted that similar deposition of white materials were observed on the inorganic zinc coated coupons in ICET Test 2, which had chemical conditions similar to these tests.

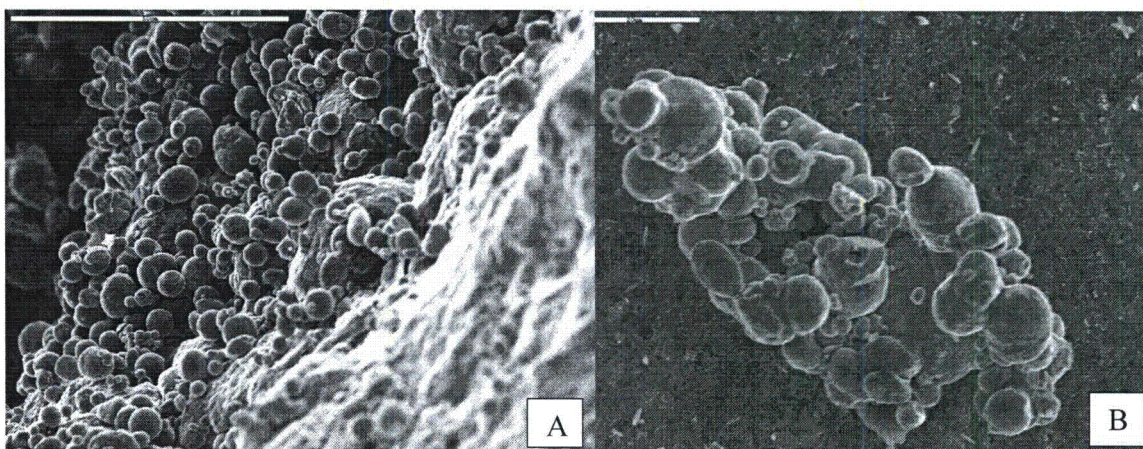


Figure 28 – SEM images of (A) zinc granules contained within stainless steel mesh bags, and (B) product captured on an in-line membrane filter after 24 hours of testing. EDX analysis of capture material indicates it is likely zinc granules.

The white material was scraped from the galvanized steel plates and subjected to scanning electron microscopy (SEM) with energy dispersive X-ray spectrometry (EDX), X-ray photoelectron spectrometry, inductively-coupled plasma spectrometry (ICP) following acid digestion, and X-ray diffraction (XRD) analysis. The analyses indicate that the material is a crystalline form of a zinc phosphate solid similar to the mineral hopeite with the chemical composition $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$. A SEM image of the crystalline materials is shown in Figure 29-B. The thermodynamic equilibrium dissolution coefficient ($\log K_{\text{SP}}$ value) present in the Visual MINTEQ database for this material suggests it is very insoluble.

Evaluation of Debris Bed Response to WCAP Precipitate Addition

The primary objective of this CHLE preliminary test series was to select a bed preparation protocol suitable for initiating the 30-day baseline performance tests. Important attributes in selecting a debris bed included mechanical integrity, reproducibility, chemical detection threshold sensitivity, and time-response sensitivity. The tests evaluated the NEI pressure-washed and the blender-prepared debris beds at 0.1 and 0.01 ft/s approach velocities. The tests were conducted with circulation solutions of either deionized water or deionized water with boric acid and trisodium phosphate (TSP). Some preliminary tests also considered the use of green silicon carbide as particulate debris, the use of a double leaf-shredded fiber debris bed, and deionized water with boric acid and sodium tetraborate. WCAP precipitates were added directly in the head loss columns or in the CHLE corrosion tank.

Testing found that the NEI fiber preparation method resulted in very consistent debris beds. Incremental additions of fiber resulted in a linear increase in bed thickness and head loss. Repeated tests resulted in similar increases in bed thickness and head loss, as shown in Figures 30, 31, and 32. The blender method resulted in less consistent debris beds. The increase in head loss with additions of fiber was non-linear. In addition, changing the approach velocity and returning it to the original velocity resulted in significant increases in head loss. After a threshold quantity of fiber was introduced into the column, the head loss through the fiber-only bed increased rapidly to over 50 inches at both 0.1 and 0.01 ft/s, as shown in Figures 33 and 34.

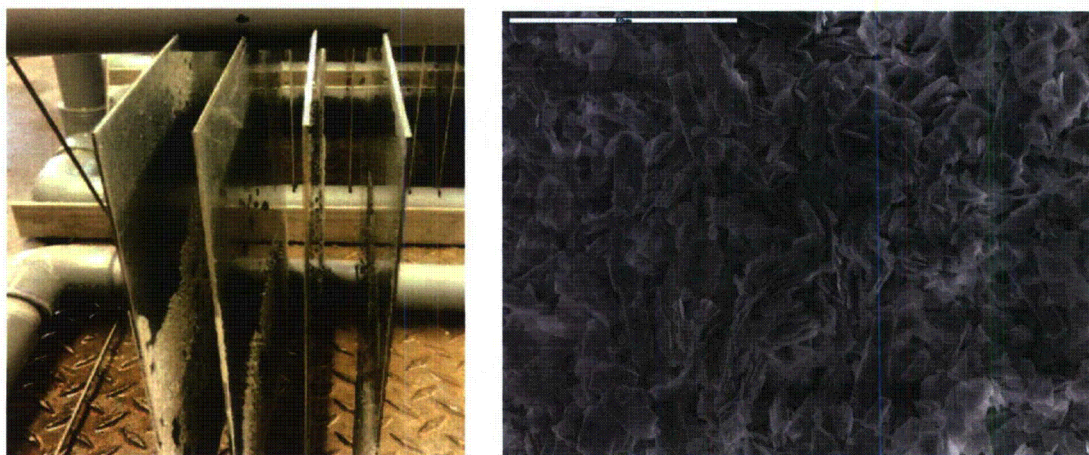


Figure 29 – (A) White material present on the submerged galvanized coupons at the conclusion of the 30-day LBLOCA test, and (B) SEM images of the same white material.

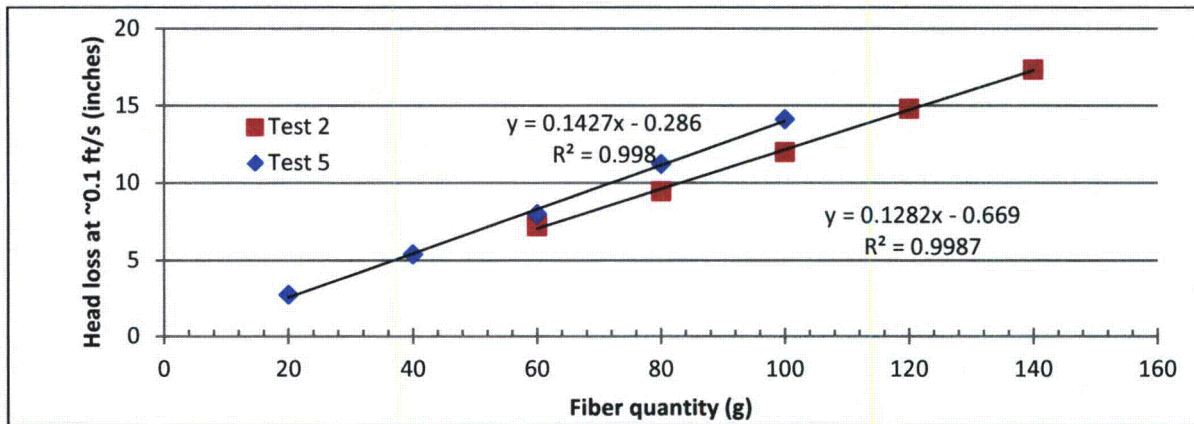


Figure 30 – Head loss through NEI pressure-washed debris beds at approach velocity of 0.093 ft/s in Test 2 and 0.1 ft/s in Test 5.

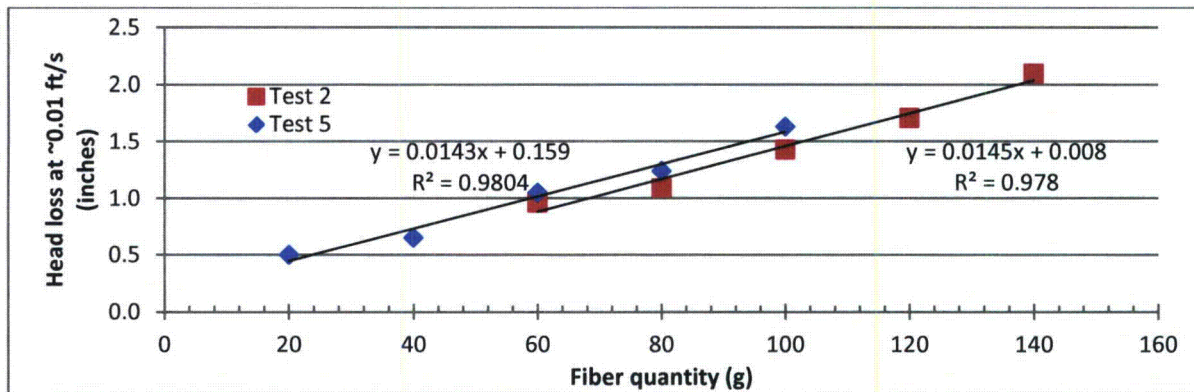


Figure 31 – Head loss through NEI pressure-washed debris beds at approach velocity of 0.01 ft/s in Tests 2 and 5.

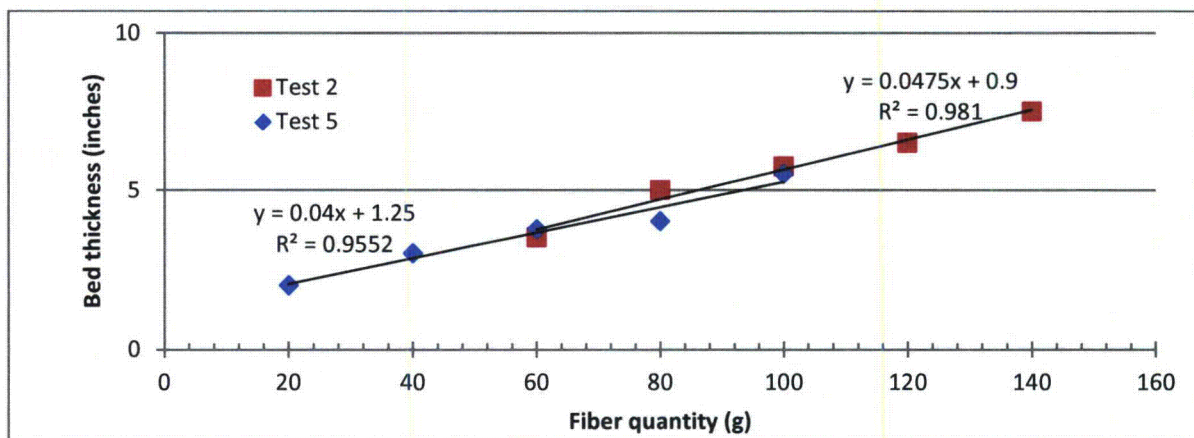


Figure 32 – Fiber bed thickness of NEI pressure-washed debris beds at approach velocity of 0.1 ft/s in Tests 2 and 5.

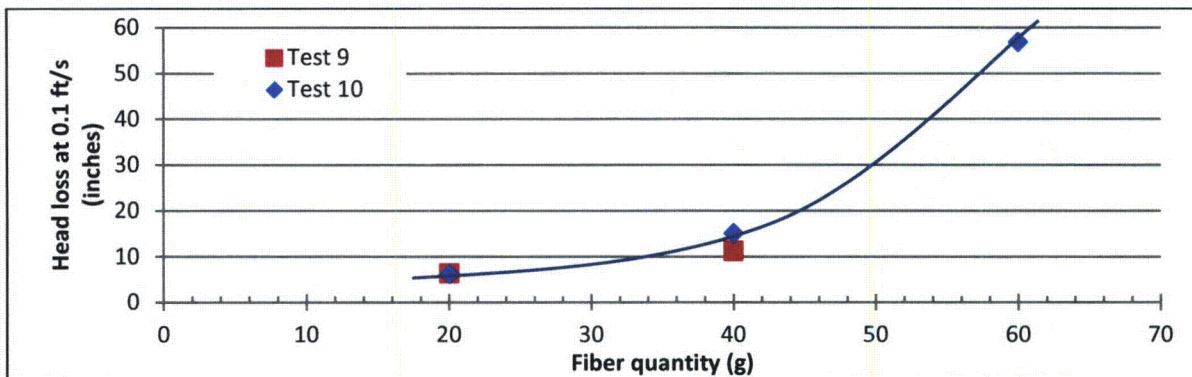


Figure 33 – Head loss through blender-processed debris beds at approach velocity of 0.1 ft/s in fiber beds prepared with a blender (Tests 9 and 10).

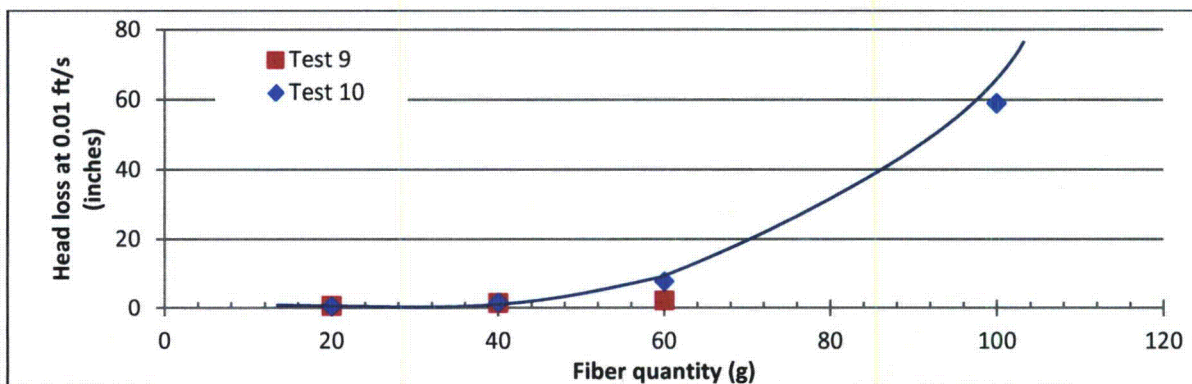


Figure 34 – Head loss through blender-processed debris beds at approach velocity of 0.01 ft/s in fiber beds prepared with a blender (Tests 9 and 10).

The increase in head loss caused by cycling the velocity low and high through the blender-prepared debris bed was as much as 80 percent, as shown in Figure 35.

The NEI and blender fiber preparation methods were both effective at capturing WCAP precipitates, but the blender-prepared fiber was more effective. The addition of WCAP precipitate in small increments resulted in non-linear head loss behavior. The first additions, if small, resulted in small increases in head loss. Once a threshold quantity that coated the leading surface of the bed was reached, however, head loss increased rapidly until the test had to be terminated.

For both debris beds, the WCAP precipitates were added in batches corresponding to 0.45 g of Al directly to the recirculating head loss column, which resulted in a bed loading rate of 24.7 g/m² as Al for each batch. As shown in Figure 36 for the NEI bed, 4 batches of WCAP precipitate were added with only marginal increases in head loss, resulting in an aluminum loading rate into the bed of 98.8 g/m² as Al. An additional loading of 12.3 g/m² as Al for a total loading of 111 g/m² as Al, resulted in a rapid increase in head loss. As is demonstrated in Figure 37, these results were reproducible over multiple tests.

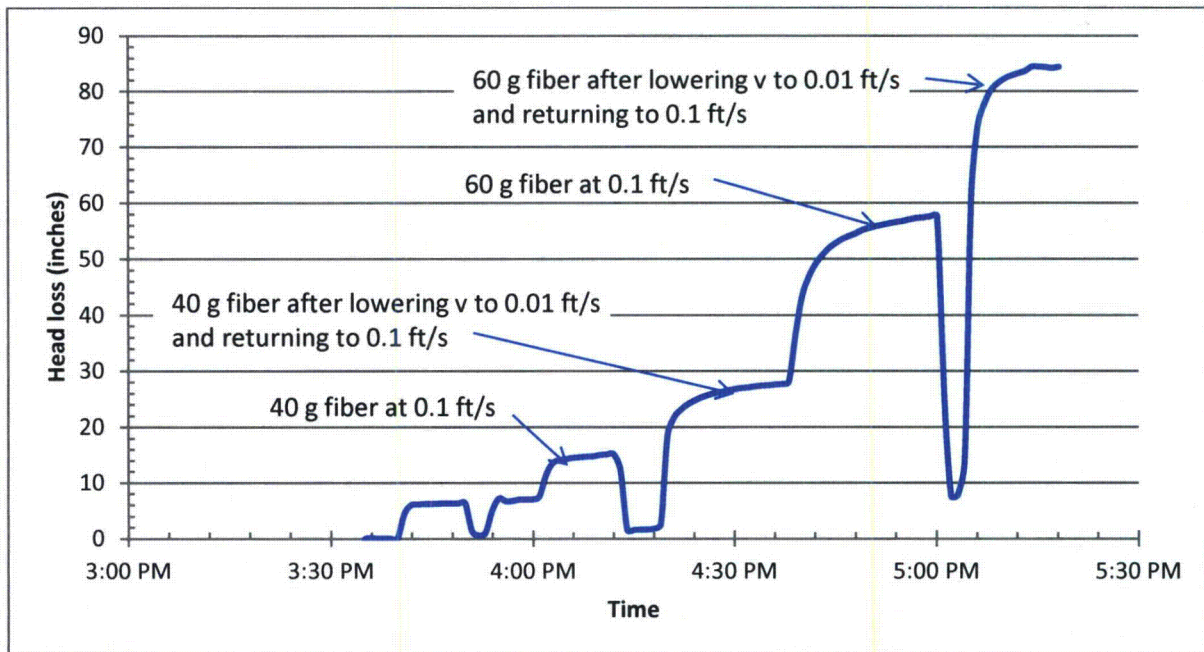


Figure 35 – Head loss through a blender-prepared fiber debris bed in Test 10.

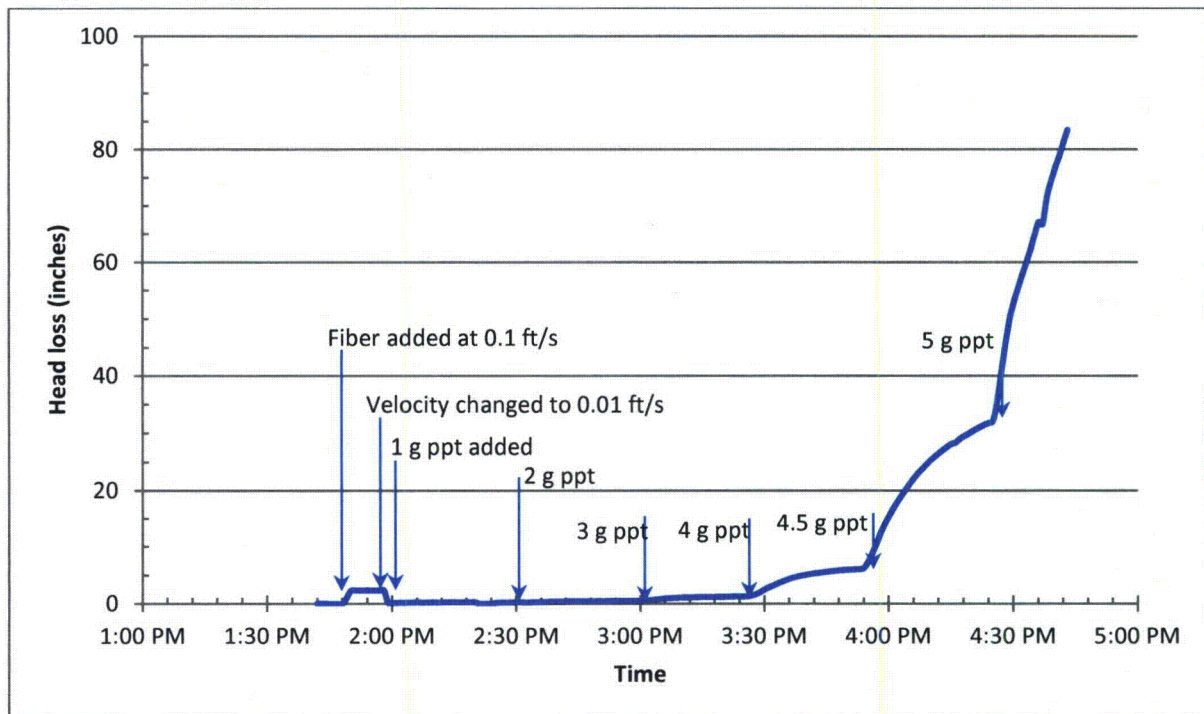


Figure 36 – Head loss after addition of 1 g increments of WCAP precipitate introduced into a NEI pressure-washed debris bed (Test 6). Quantities refer to amount of AlOOH precipitate prepared according to the WCAP recipe.

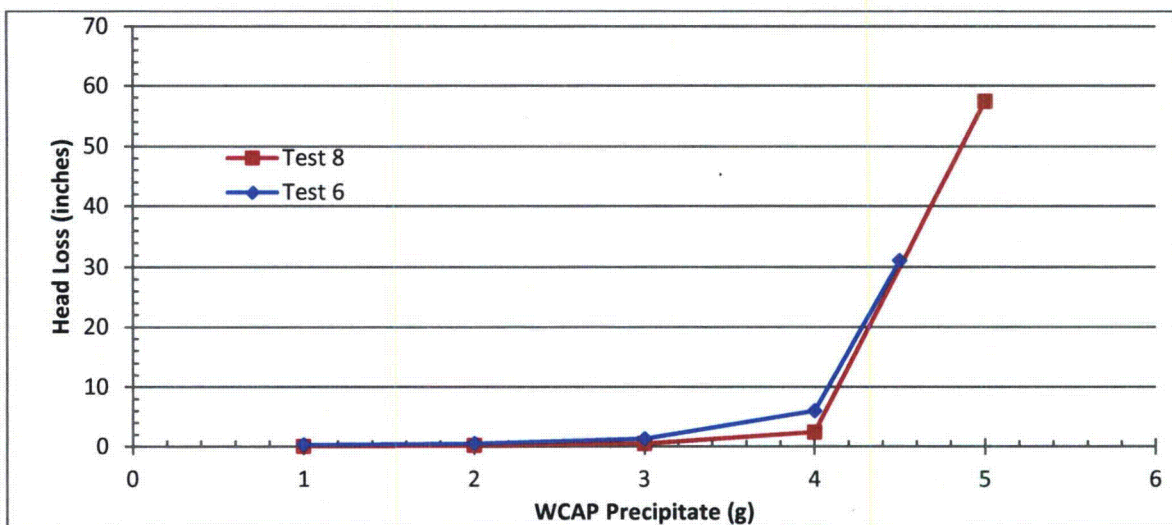


Figure 37 – Comparison of head loss after addition of WCAP precipitate introduced into a NEI pressure-washed debris bed in Tests 6 and 8.

For the blender-processed bed, the first batch of precipitate caused a rapid increase in head loss, indicating that the threshold for causing head loss in this type of bed is 24.7 g/m^2 as Al or less. In tests conducted at ANL, head loss increased rapidly when the aluminum loading reached 13.3 g/m^2 as Al. The results of these tests are consistent with the ANL work for the blender-prepared bed, but demonstrate that the NEI pressure-washed debris bed is less sensitive to the presence of chemical precipitates than the blender bed under these conditions.

Additional tests were conducted in which the WCAP precipitates were added into the CHLE corrosion tank at high temperature instead of directly into the head loss columns at room temperature. An important consideration in the addition of precipitates into the CHLE tank is that the circulation time is much greater. The circulation time in the closed-loop head loss columns was 8.5 minutes, whereas the circulation time when the CHLE corrosion tank was in operation was 110 minutes. This difference in circulation time was not taken into account when the tests were conducted. Two to three pool turnovers were allowed between precipitate additions in the closed-loop head loss column tests, but multiple batches of precipitate were added in less than one pool turn-over in the tank tests. Thus, it is not possible to determine the quantity of precipitate that would cause head loss to increase rapidly in the tank tests from these tests.

The results described in this section demonstrate that the NEI pressure-washing method resulted in more stable and reproducible debris beds than the blended bed method in relatively short (several hour) head loss tests. However, the blended debris beds experienced greater head loss when precipitates prepared according to the WCAP protocol were introduced directly into the head loss assemblies, leading to the conclusion that the blended fiber debris beds are more sensitive detectors for the presence of precipitates.

Evaluation of Long-Term Aluminum Nitrate Addition to Debris Beds

The original objective of this test series was to establish the baseline performance (without the addition of corrosion materials) of the debris bed to be used for the 30-day CHLE tests with corrosion materials in place. Based on discussions with the NRC, the selected debris bed type for the 30-day testing was the blender-processed bed. Within a few days of operation, however, the blender-prepared debris beds exhibited instabilities and inconsistent performance between parallel columns, as detailed later in this section. Thus, the objective of the test series was modified to additionally evaluate the performance of the debris bed with the addition of aluminum nitrate at a slow rate to simulate the introduction of aluminum into the solution as the result of corrosion processes. In addition, a second test was conducted using NEI-processed debris beds so that the two beds could be compared. The testing program was conducted from 28 June 2012 to 24 July 2012.

Throughout the tests, the chemical system in the tank was prototypical of the post-LOCA chemical environment at STP; the chemicals included boric acid, trisodium phosphate, lithium hydroxide, hydrochloric acid, and nitric acid. The support screen used was prototypical of the ECCS strainers at the STP plant. A temperature profile characteristic of a medium-break LOCA as predicted by MELCOR and RELAP-5 was used. The approach velocity to the debris beds was 0.01 ft/s to be consistent with the strainers at STP.

As noted above, the blender-processed debris beds were not reproducible between columns. After 6 days of operation, the normalized head loss (normalized to 20 °C based on both viscosity and density corrections) varied from 1.6 inches of water to 100 inches of water through debris beds, as shown in Figure 38. It is important to note that the columns were in parallel operation so that each column was circulating the same water at the same rate. This degree of inconsistency between columns was determined to be too excessive to allow assessment of the impact of chemical precipitates, since it was clear that factors other than chemical precipitates could lead to significant differences in head loss.

An inspection of the debris beds after the test was complete revealed that the blender-prepared beds formed small, dense nodules of fiber at the base of the fiber bed, immediately adjacent to the perforated support plate, as shown in Figure 39. The nodules formed a dimple pattern that matched the pattern of holes in the perforated plate, indicating that the smaller fibers formed by the blending process were able to form a more dense fiber mat in a localized area. The difference in head loss among the three columns with the blended fiber preparation appears to be due to a trace amount of dirt or other material that collected in the small, dense fiber nodules at the base of the fiber bed. The debris bed with the highest head loss visually had the greatest amount of darker material present in the nodules. The fiber beds were visibly clean through the rest of the depth, suggesting that little or no head loss occurred through the bulk of the depth of the fiber bed and that nearly all of the head loss occurred in the fiber where it contacted the perforated plate, indicating significant nonhomogeneity to the porosity and head loss characteristics of the bed.

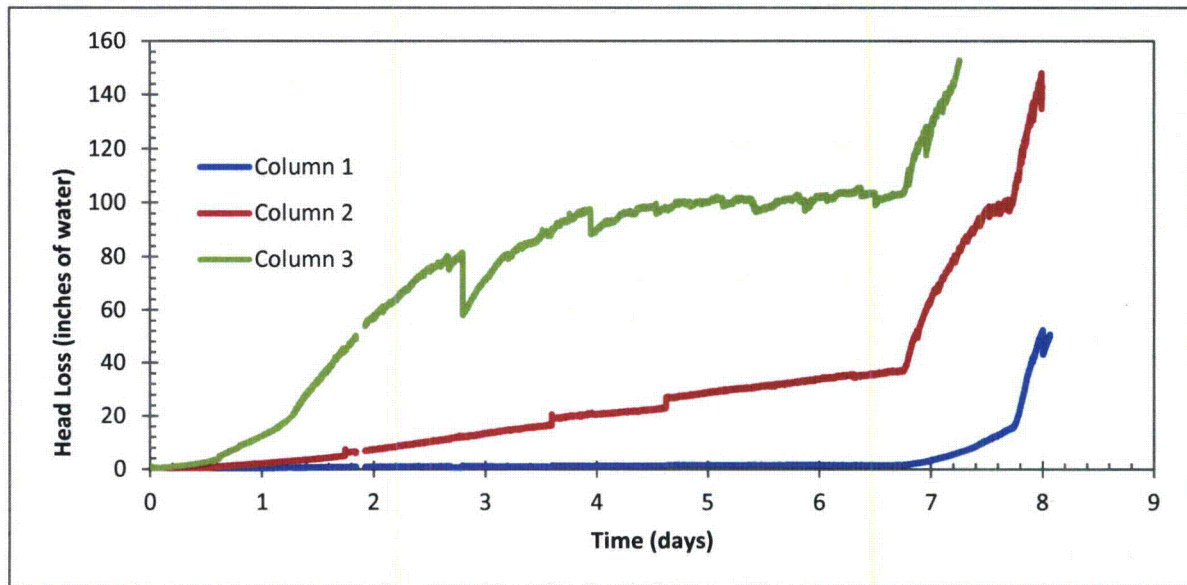


Figure 38 – Normalized head loss through fiberglass debris beds prepared by chopping in a blender (normalized to 20 °C). Aluminum nitrate addition started at about 6.75 days.

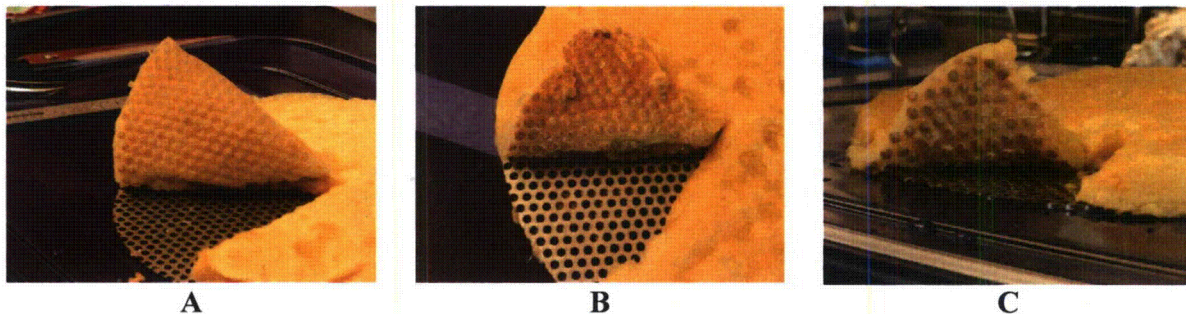


Figure 39 – Dimple pattern from the support plate on the bottom side of the blended fiber debris beds in (A) Column 1, (B) Column 2, and (C) Column 3. The dimples in Column 3 are darker than in Column 1. Also, the cross section of the debris bed, most evident on Column 3, appears clean throughout the entire depth of the debris bed.

The fiber beds prepared with the NEI pressure-washing method were reproducible between columns. After 6 days of operation, the normalized head loss remained less than 0.5 inches of water, as shown in Figure 40. Similar behavior continued until the test was terminated after 12 days. The fiber beds prepared with the NEI pressure-washing method did not form the dense nodules of fiber that were observed with the blended fiber beds. The absence of these nodules and the reproducible behavior of the NEI beds lends further credibility to the conclusion that these nodules were responsible for the non-reproducible behavior of the blended fiber beds.

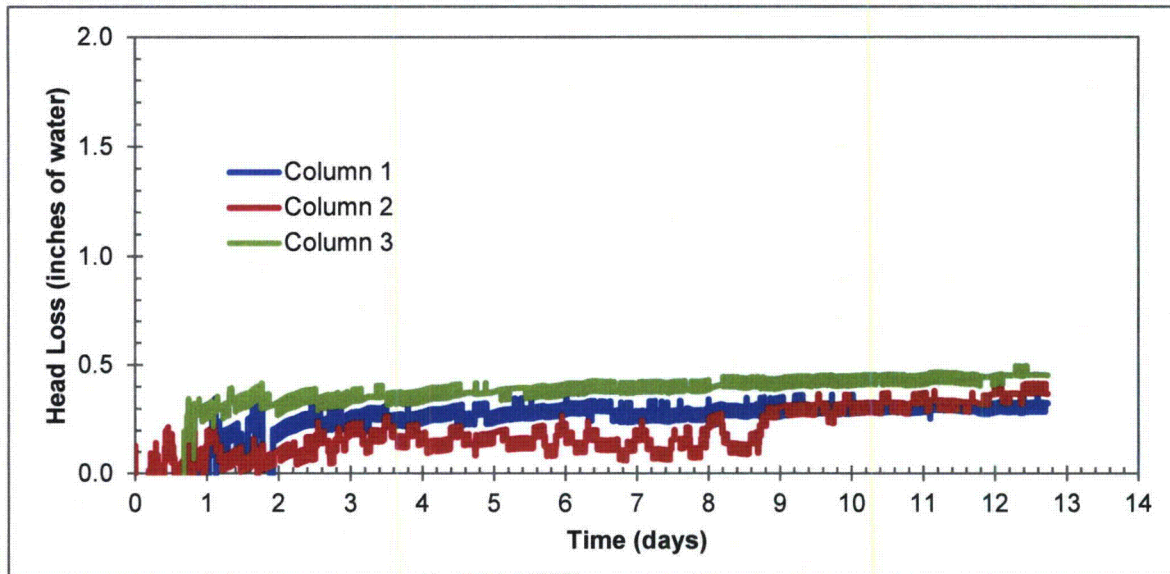


Figure 40 – Normalized head loss through fiberglass debris beds prepared using the NEI pressure-washing method (normalized to 20 °C).

The blended fiber preparation method resulted in shorter fibers (often called “shards” or “fragments”) than with the NEI pressure-washing method, which may have led to the ability of the bed to form the dense nodules at the holes in the perforated plate. The shorter fibers led to a more compact debris bed, as shown earlier in Figure 6. Low porosity nodules are formed by local bed compaction, enabled by the mobility of short fiber shards formed during the chopping procedure. Local compaction in regions of flow acceleration near the strainer penetrations is further enabled by loosely aggregated beds formed under very low approach velocity.

The debris beds did not change thickness significantly over the course of the test, which lasted over 8 days for the blended fiber debris bed and over 12 days for the NEI fiber debris bed. Further, minimal differences in thickness were observed between beds despite the wide variation in measured pressure loss. The lack of change in bed thickness, coupled with the visually clean nature of the debris beds, lends credibility to the conclusion that the head loss associated with the blended fiber debris bed was due to localized conditions at the perforated plate.

After 6.75 days of operation, aluminum nitrate solution was bled into the system at a slow rate to simulate the addition of aluminum via corrosion processes. It was intended to add the aluminum nitrate at a sufficiently low rate to prevent the formation of precipitates until the entire solution reached the saturation concentration, but insufficient mixing at the point of addition allowed localized higher concentration conditions that caused precipitation to occur. A significant fraction of the aluminum that was added to solution formed a precipitate, as indicated by turbidity measurement and supported by total and filtered aluminum analyses. The addition of 1 mg/L of aluminum in solution caused the formation of in-situ precipitates that caused head loss through the blender-processed debris beds. Since the bed in column 3 was already at 100 inches

of normalized head loss (Figure 38), this addition was sufficient to reach the terminal head loss condition in that column. Column 2, which had been at about 38 inches of normalized head loss, increased to about 100 inches of head loss and appeared to be leveling off. Column 1 increased from 1.6 inches to about 18 inches. After 23 hours (12.5 pool turnovers), an additional 5 mg/L (6 mg/L total) caused sufficient head loss to terminate the test.

In contrast to the blender-processed debris bed, the addition of up to 40 mg/L of aluminum over a period of 6 days was not sufficient to cause head loss through the NEI fiber debris beds, as shown in Figure 34. However, in tests reported in the previous section, the same amount of aluminum in the form of pre-formed WCAP precipitates caused extensive head loss (Figure 36) that terminated a similar test within 3 hours (1.6 pool turnovers). These results indicate that precipitates formed in-situ through the addition of aluminum nitrate at a slow rate have significantly different characteristics from those of the pre-formed WCAP precipitates.

Particle size analyses indicate that the size of precipitates formed in-situ are up to 10 times smaller than the pre-formed WCAP precipitates with similar solution conditions (0.17 μm versus 1.6 μm in diameter, as shown in Table 7). This significant difference in size appears to be sufficient to cause the pre-formed WCAP precipitates to be retained by the NEI fiber debris beds but allow the in-situ precipitates to pass through the NEI fiber debris beds. The results indicate that head loss may be less significant than indicated by the use of pre-formed WCAP precipitates, depending on the solution chemistry and the filtration characteristics of the debris bed. The small size of the colloids formed in-situ is consistent with the constituent particle diameter reported in NUREG/CR-6915 [21] (which reported a diameter of 0.13 μm).

Similar results were also observed in testing at ANL [19]. In tests conducted with blended-fiber beds, aluminum added at a concentration of 1.5 ppm (filter loading rate of 13.3 g/m^2 as Al) was sufficient to plug the debris bed when added as pre-formed WCAP precipitates. The researchers at ANL found that aluminum precipitates formed using a different recipe, in water that contained boron and silicon, form particles in the range of 0.1 to 0.3 μm in diameter, considerably smaller than the particles observed when precipitates were formed using the standard WCAP protocol. When the alternate precipitates were introduced into a head loss loop containing a blended-fiber bed, no head loss occurred even at aluminum concentrations as high as 33 ppm (filter loading rate of 260 g/m^2 as Al). The ANL researchers concluded that "particles less than 0.5 μm in size do not get trapped in ANL's reference NUKON bed and are therefore not effective at producing head loss across the ANL fiber-only debris bed." [19]. Based on the work conducted at ANL, the ability of colloidal aluminum precipitates to pass through a debris bed without being captured does not appear to be limited to the NEI-processed debris bed, but can also happen with blender-processed beds under appropriate conditions.

Summary and Conclusions

The primary conclusions of the CHLE tests in 2012 are related to the outcome of the 30-day MBLOCA test. The significant conclusions of the testing program can be summarized as follows:

Table 7 – Particle size and zeta potential of aluminum hydroxide precipitates ¹

	Particle Size (μm)	Zeta Potential (mV)
Pre-formed WCAP Precipitates		
In boron/TSP water, 30 mg/L dilution	1.6	-28
In boron/TSP water, 40 mg/L dilution	1.6	-25
In boron/TSP water, 10 mg/L dilution	1.6	-27
In deionized water, 40 mg/L dilution	1.8	29
In deionized water, 10 mg/L dilution	2.5	30
In tap water	1.2	-3
In-situ Precipitates (in boron/TSP water)		
At end of test	0.17	-31
Two weeks later	0.18	-32

1. Each value given is the average of three measurements

1. Weight loss measurements and calculations indicated that a total of 0.90 g of aluminum metal corroded during the CHLE 30-day MBLOCA test. This quantity of material lost corresponded to corrosion rates of 7.1 g/m² as Al for submerged aluminum and 2.4 g/m² as Al for aluminum exposed to containment sprays over a 30 day period. The observed results are in general agreement with the results from ICET Test #2, which was conducted under similar chemistry and pH conditions, but with different aluminum material and temperature profile. The corrosion rates are less than 3 percent of the rates calculated for a design basis LOCA using the WCAP-16530-NP spreadsheet, indicating that significantly less aluminum will be available to form chemical products in a MBLOCA than predicted for a design basis LOCA.
2. The concentration of aluminum measured in solution in the CHLE tank during the MBLOCA test was 0.28 mg/L, in general agreement with the low rate of corrosion. As a point of reference, the concentration of aluminum predicted by the WCAP-16530-NP spreadsheet for the design basis LOCA was 32.9 mg/L.
3. The turbidity in the tank solution peaked at the beginning of the MBLOCA test at approximately 0.6 NTU and gradually decreased to about 0.3 NTU at the end of the test. A similar trend was observed in tests that did not have corrosion coupons in the tank, indicating that this level of turbidity was due to particles present in the tank at the beginning of the test. The fact that turbidity did not increase supports a conclusion that precipitation of corrosion products in the bulk solution did not occur.

4. Measurements of filtered and total aluminum in solution were essentially identical to each other over the duration of the MBLOCA test. The fact that there was no difference between the filtered and unfiltered samples supports a conclusion that there was no precipitated aluminum greater than 0.45 μm (the pore size of the filter) circulating in the solution. Similar results were obtained for calcium and silicon.
5. The measured aluminum and calcium concentrations were below the solubility limits for aluminum hydroxide and calcium phosphate, respectively, as calculated by Visual MINTEQ for the conditions representative of STP. Work conducted at ANL has indicated that solubility of amorphous aluminum hydroxide calculated by Visual MINTEQ was a good indicator of the boundary at which precipitation occurs. These results provide a rationale for why no precipitates formed and are generally supportive of the observed results.
6. The normalized head loss through all three of the NEI-processed debris beds remained below 0.5 inches of water column for the duration of the 30-day test. The normalized head loss through the blender-processed debris beds was marginally higher than the head loss through the NEI-processed debris beds in all 3 columns when exposed to the tank solution for 2 days at the end of the 30-day MBLOCA test. However, the normalized head loss was still below 1 inch in all 3 columns. While questions have been raised regarding the appropriate debris bed to use in these experiments, these results are consistent with experiments conducted at ANL, which used blender-prepared debris beds. Based on the measured aluminum concentration in solution, the aluminum loading rate on the CHLE debris beds would have been 5.8 g/m^2 as Al if precipitates had formed and would be 1.7 g/m^2 as Al based on the surface area of the strainers at the STP plant. In testing at ANL, introduction of pre-formed precipitates at a concentration of 0.5 ppm of Al and aluminum loading rate of 4.4 g/m^2 as Al caused only a minor increase in head loss. In the ANL work, plugging of the debris bed did not occur until the aluminum loading reached 13.3 g/m^2 as Al. Similarly, in small-scale chemical effect testing described in NUREG/CR-6868, additional head loss due to chemical precipitates did not begin to occur until the aluminum concentration was 2.7 mg/L and the loading rate was 3.5 g/m^2 as Al. Comparison to these previous results supports a conclusion that little or no increase in head loss would likely have occurred in these tests regardless of what debris bed was used, even if precipitates had formed.
7. The testing of the ECCS Sure-FlowTM strainer module subjected to prototypical debris from the STP plant by Alden in 2008 resulted in additional head loss due to chemical precipitates of 4.75 ft, an increase of 2.2 times the head loss due to non-chemical debris. The chemical precipitate loading to the system that caused this head loss was screen loading rate of 990 g/m^2 of Al and of 190 g/m^2 of Ca. These quantities are substantially higher than the precipitate loading rates observed in the CHLE work for a 6-inch cold leg MBLOCA. Head loss was observed as soon as the first batch of precipitates was added in the Alden test, but that first addition corresponded to a loading rate of 77 g/m^2 of Al. The substantial difference in concentrations and loading rates provides an explanation for why an increase in head loss was observed in the Alden testing and not in the CHLE tests.
8. The results of the LBLOCA test was similar to the MBLOCA test in many respects, such as generally low concentration of metal ions in solution, low and gradually declining turbidity

over the duration of the test, and minimal levels of head loss. However, some differences were observed. The head loss did increase during the LBLOCA test, whereas it did not in the MBLOCA test. The constituents that contributed to the increase in head loss could not be identified, but may have been zinc granules circulating in solution or zinc phosphate that formed during the test. The concentrations of metal ions were generally lower in the LBLOCA test even though predictions based on corrosion rates suggest that the concentrations should have been higher. The presence of zinc in solution in the LBLOCA test may have had an inhibitory effect on the corrosion and release rates of other materials and should be explored in further testing. The zinc phosphate material that formed was identified as a crystalline material with the chemical formula $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$.

Based on the low quantities of aluminum and calcium released into solution and the fact that the resulting concentrations appear to be below the saturation concentrations for aluminum hydroxide and calcium phosphate, it is expected that no precipitates will form for a LOCA in a 6-inch or smaller break at the STP plant. Furthermore, if precipitates were to form, they would be unlikely to cause a significant increase in head loss. As a result, chemical precipitates are expected to have no effect on the ECCS strainers at the STP plant for all LOCAs smaller than a 6-inch break. Although additional testing is needed, the similarity of the results between the MBLOCA and LBLOCA tests suggests that it may be appropriate to extend the conclusions of the MBLOCA test with respect to the effect of chemical precipitates on ECCS strainer head loss to include breaks on pipes up to 15 inches in diameter.

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